**United States Environmental Protection Agency**

*Region 10, 1200 Sixth Avenue, Seattle WA 98101*

# COLUMBIA RIVER BASIN FISH CONTAMINANT SURVEY

# VOLUME 4. QUALITY ASSURANCE SUMMARY TO THE PROJECT FINAL PLAN

**Revision: 3.2**
**November 9, 2001**

# DISCLAIMER

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# EXECUTIVE SUMMARY

This Quality Assurance Summary to the Project Final Report represents the conclusion of the data collection and data quality assessment phase of a U.S. Environmental Protection Agency (EPA) study to assess chemical contaminant exposure and risks from consumption of Columbia River fish by four Native American Tribes (Confederated Tribes of the Umatilla Indian Reservation, Confederated Tribes of the Warms Springs Reservation, Nez Perce Tribe, and Yakama Nation) and other people in the Columbia River Basin. These Tribes are also referred to as Columbia River Treaty Tribes. Phase One of this study was a fish consumption study of Tribal members which was completed in October of 1994 by the Columbia River Inter-Tribal Fish Commission (CRITFC). This current phase of the study (referred to as Phase Two), consists of evaluating tissue contaminant data representing resident and anadromous fish species that are typically caught by Tribal fisheries in the Columbia River Basin and consumed by Tribal members. The information from both phases of this exposure study is being used to assess the potential health impacts from consuming contaminants in Columbia River fish. A Quality Assurance Project Plan (QAPP) was prepared and approved in 1996 by EPA Region 10 Office of Environmental Assessment as a written project plan for Phase II of the study. The purpose of this Quality Assurance Summary is to provide data users with sufficient project information and data quality information from which data useability decisions can be determined.

The objectives of the QAPP required a high level of communication and teamwork among EPA and Tribal project members. Because the length of the sampling period and analytical work extended over a three year period, procedures for collection of samples, grinding and compositing of fish, and the analysis of target compounds had to be consistent in order to have a comparable database of chemical measurements.

The objectives for Phase II, as discussed in the QAPP, were as follows:

1. Measure fish contaminant levels for species and fishing locations being utilized by CRITFC member Tribes to provide, in conjunction with the CRITFC fish consumption report, an assessment of fish consumption among individuals of the Columbia River Basin and these Tribes as an exposure route to residues of toxic waterborne chemicals.

2. Use the information derived from the exposure assessment to estimate potential health risks to fish consumers in the Columbia River Basin. Tribal staff will evaluate exposure and risks to members of their individual Tribes.

This Quality Assurance Summary to the Project Final Report only presents documentation on the collection and analysis of project samples and the data quality assessment of project measurements. Other volumes of the Final Project Report present information on the potential health risks to fish consumers in the Columbia River Basin.

From a quality assurance and data quality objective viewpoint, this project was most challenging. The QAPP required the collection of approximately 2,500 fish (not counting the Eulachon

(smelt)) at 65 sampling locations. The grinding and compositing of fish into 302 nearly homogenous tissue samples required heroic dedication, three tissue grinders, and many watts of electricity. All analytical sample extraction and preparation procedures required modifications to accommodate project samples, some of which had percent lipid values of up to 21%. Project risk assessment objectives required that we measure many target compounds in which analytical methods were not available. Three new EPA analytical methods were employed for the first time on project fish composite samples. The QAPP required the measurement of up to 210 target compounds in most project samples. This resulted in a project measurement database of approximately 51,000 measurements. Approximately 11,800 target compounds were detected and measured in project samples. There were several target compounds which were measured in project samples which have not been previously reported as being present in Columbia River basin fish. Among the 24 newly measured compounds reported in project data, five were pesticides, three were brominated diphenyl ether fire retardant isomers, ten were PCB congeners, and six were semivolatile compounds. Generally, the measurement of these new target compounds were due to the use of new analytical methods and the use of newly developed sample extract clean-up procedures.

Precision from the measurement of blind field duplicate samples and precision and accuracy from the measurement of matrix spike / matrix spiked duplicate (MS/MSD) samples demonstrated that the project team was successful in meeting analytical objectives of the QAPP. A total of 9 blind field duplicate samples, 6 performance evaluation fish reference samples (for PCDDs/PCDFs and PCB congeners) and approximately 20 sets of MS/MSD samples were measured to demonstrate that project precision and accuracy requirements were met. Project quality assurance measurements and laboratory quality control measurements indicated that project data, as has been qualified in project data validation reports, are fully useable to assess potential health risks due to exposure to contaminants through fish consumption.

As a result of the tremendous help and work of Tribal members and a dedicated EPA/Tribal sampling team, the sample collection objectives of the QAPP were accomplished. Overall, the ambitious data quality objectives of the QAPP were also accomplished. This project has produced a body of comparative chemical data which can be used by Tribal Members and risk assessors to assess chemical contaminant exposure and risks from consumption of Columbia River fish.

Robert G. Melton, Ph.D., Chemist
EPA Project Quality Assurance Manager
Office of Environmental Assessment
EPA Region 10

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# ACRONYMS

| | |
|---|---|
| %R | percent recovery |
| µl | microliter |
| Abs | absolute value of a number |
| AED | atomic emission detector |
| AERF | atomic emission response factor |
| Al | aluminum |
| Am | americium |
| As | arsenic |
| ASTM | American Society of Testing and Materials |
| AXYS | AXYS Laboratory at Sidney, BC Canada |
| CAS | Chemical Abstracts |
| Cd | cadmium |
| CDDs | chlorinated dibenzodioxins |
| CDFs | chlorinated dibenzofurans |
| CFR | Code of Federal Regulations |
| CIC | compound independent calibration |
| Co | cobalt |
| COC | chain of custody |
| COMP | compound |
| Cr | chromium |
| CRITFC | Columbia River Inter-Tribal Fish Commission |
| Cs | cesium |
| CS1 | calibration solution number one |
| CS3 | calibration solution number three |
| CTUIR | Confederated Tribes of the Umatilla Indian Reservation |
| CTWS | Confederated Tribes of the Warm Springs Reservation |
| Cu | copper |
| CVAA | cold vapor atomic absorption |
| D | duplicate field sample |
| DCM | dichloromethane |
| DDD | 1,1'-(2,2-dichloroethylidene)bis-(4-chlorobenzene) |
| DDE | 1,1'-(dichloroethylidene)bis(4-chlorobenzene) |
| DDT | 1,1'-(2,2,2-trichloroethylidene)bis(4-chlorobenzene) |
| DQA | data quality assessment |
| DQO | data quality objective |
| Dups | duplicate samples |
| E | The reported value is an estimate because of the presence of an interference. An explanatory note is provide in the data validation report. |
| ECD | electron capture detector |
| EDL | experimental detection limit |
| EI | electron impact |
| EPA | U. S. Environmental Protection Agency |
| Eu | europium |

| | |
|---|---|
| EVS | EVS Environmental Consultants |
| F1 | fillet from right side of fish |
| F2 | fillet from left side of fish |
| Fe | iron |
| FS | fillet with skin |
| FW | fillet without skin |
| g | gram |
| GC | gas chromatography |
| GCP | guaiacols and chlorinated phenols |
| GIS | graphical information system |
| GPC/SG | gel permeation chromatography / silica gel |
| GPS | global positioning system |
| HP | Hewlett Packard |
| HRGC | high resolution gas chromatography |
| HRMS | high resolution mass spectrometry |
| ICP/AED | inductively coupled plasma / atomic emission spectrometry |
| ICP/MS | inductively coupled plasma / mass spectrometry |
| ID | identification number |
| IDFG | Idaho Department of Fish and Game |
| IDL | instrumentation detection limit |
| IPR | initial precision and recovery standard |
| J | The analyte was analyzed for and was positively identified, but the associated numerical value may not be consistent with the amount actually present in the environmental sample. |
| K | potassium |
| kg | kilogram |
| La | lanthanum |
| Lat | latitude |
| LRMS | low resolution mass spectrometry |
| Lon | longitude |
| MDC | minium detection concentration |
| MDL | method detection limit |
| ml | milliliter |
| ML | method limit |
| Mn | manganese |
| MS | matrix spike |
| MS/MSD | matrix spike/matrix spike duplicate |
| MSD | matrix spike duplicate |
| N | The analysis indicates the presence of an analyte for which there is presumptive evidence to make a tentative identification. |
| Na | sodium |
| NAERL | EPA National Air and Radiation Environmental Laboratory |
| Nb | niobium |
| ng/ml | nanogram per milliliter |
| Ni | nickel |
| NIST | National Institute of Standards and Technology |

| | |
|---|---|
| NPDES | National Pollutant Discharge Elimination System |
| NRCC | National Research Council of Canada |
| OPR | on-going precision and recovery standard |
| OR | Oregon |
| ORFW | Oregon Fish and Wildlife |
| OW | EPA Office of Water |
| PAHs | polycyclic aromatic hydrocarbons |
| PAR | precision accuracy and recovery standard |
| Pb | lead |
| PBDEs | polybrominated diphenyl ethers |
| PCBs | polychlorinated biphenyls |
| PCDDs/PCDFs | polychlorinated dibenzodioxins / polychlorinated dibenzofurans |
| PCDEs | polychlorinated diphenyl ethers |
| PE | performance evaluation sample |
| Pest | pesticide |
| PFK | perfluorokerosene |
| pg/l | picogram per liter |
| PQL | practical quantitation limit |
| pg/kg | picogram per kilogram |
| Pr | praseodymium |
| Pu | plutonium |
| QA | quality assurance |
| QA/QC | quality assurance/quality control |
| QAM | quality assurance manager |
| QAPP | quality assurance project plan |
| QMP | quality management plan |
| R | The sample results are rejected due to serious deficiencies in the ability to analyze the sample and meet quality control criteria. The presence or absence of the analyte cannot be verified. |
| Ra | radium |
| RPD | relative percent difference |
| RSD | relative standard deviation |
| Ru | ruthenium |
| SDG | sample delivery group |
| SI/COC | sample identification / chain of custody |
| SIM | selected ion monitoring |
| SOP | standard operating procedure |
| SOW | statement of work |
| Sr | strontium |
| STC | tissue screening concentrations |
| SV | semivolatile |
| SW | EPA Office of Solid Waste |
| TAL | target analyte list |
| Tc | technetium |
| TCDD | tetrachlorinated dibenzodioxin |
| TCDF | tetrachlorinated dibenzofuran |

| | |
|---|---|
| TCL | target compound list |
| TIC | tentatively identified compound |
| TMDL | total maximum daily load |
| U | The analyte was analyzed for, but was not detected above the sample quantitation limit. The associated numerical value is based upon the lowest calibration point of the calibration curve and any dilutions which were made to the sample due to high concentrations or matrix effects. |
| USFWS | United States Fish and Wildlife Service |
| ug/kg | microgram per kilogram |
| ug/l | microgram per liter |
| UJ | The analysis indicates the presence of an analyte that has been "tentatively identified" and the associated numerical value represents its approximate concentration. |
| YIN | Yakama Nation |
| Ver | version |
| WA | Washington |
| WAM | work assignment manager |
| WB | whole body |
| WDFW | Washington Department of Fish and Wildlife |
| WSDE | Washington State Department of Ecology |
| WHO | World Health Organization |
| WM | wide mouth |
| Zn | zinc |
| Zr | zirconium |

# ACKNOWLEDGMENTS

The following project team members provided dedicated, coordinated work, which helped make this project to assess chemical contaminant exposure and risks from consumption of Columbia River fish by four Native American Tribes a success:

| | |
|---|---|
| EPA Project Manager | Pat Cirone |
| CRITFC Project Managers | Anne Watanabe<br>Paul Babtist Lumley, III |
| Tribal Fisheries Program Managers | |
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| Nez Perce Tribe | Silas Whitman |
| Confederated Tribes of the Umatilla Indian Reservation | Gary James |
| Confederated Tribes of the Warm Springs Reservation | Patty O'Toole |
| Tribal Project Leaders | |
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| Public Health Assessment, Yakama Nation | Chris Walsh |
| GIS Coordinator, Yakama Nation | Rolf Evenson |
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| Manager, Fisheries Division, Nez Perce Tribe | Nancy Hoefs |
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| Manager, Water Resources Division, Nez Perce Tribe | Patti Howard |
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| EPA Project Leader and Risk Assessor | Dana Davoli |
| EPA Toxicologist / Risk Assessor for Pesticide Measurements | Michael Watson |
| EPA Project QA Manager | Robert Melton |
| EPA Field Operations Manager | Dave Terpening |
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Oxbow Hatchery (IDFG) — Julie Hislop

Looking Glass Hatchery (ODFW) — Bob Lund

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Dexter Hatchery (ODFW)

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Leavenworth National Fish Hatchery (USFWS)

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Carson National Fish Hatchery (USFWS) — Bruce McCloud

Klickatat River Hatchery (WDFW) — Ed Anderson

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| EPA Regional Laboratory Project Manager | Peggy Knight |
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| GC/MS Measurements | Roy Araki |
| Metals Measurements | Tobi Braverman |
| Metals Methods Development and Measurements | Isa Chamberlain |
| AED Pesticide Measurements | Randy Cummings |
| Special Organic Separations and Data Validation | Gerald Dodo |
| Administrative Support | Barbara Haynes |
| Metals Measurements | Stephanie Le |
| Laboratory Database Manager | Tony Morris |
| Mercury Methods Development and Measurements | Kathy Parker |
| Sample Preparation and Pesticides and SV Measurements | Steve Reimer |
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| CRITFC Environmental Consultant (1996 - 1998) | Gregory Glass |
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| AXYS Laboratory QA/QC Manager | Dale Hoover |
| AXYS Laboratory HRGC/HRMS Senior Chemist | Brian Fowler |
| AXYS Laboratory Sample Preparation Supervisor | Val Scott |
| AXYS Laboratory Tissue Grinding and Homogenization | Thong Do<br>Holly Greenwood |
| EPA NAERL Chief, Monitoring and Analytical Services Branch | John Griggs |
| EPA NAERL Project Managers | Tonya Hudson<br>David Saunders |
| Project Manager For Development of EPA Method 1668 | William Telliard |

# Chapter 1.0 PROJECT DESCRIPTION

This Final Report represents the conclusion of a U.S. Environmental Protection Agency (EPA) study to assess chemical contaminant exposure from consumption of Columbia River fish by four Native American Tribes (Confederated Tribes of the Umatilla Indian Reservation, Confederated Tribes of the Warms Springs Reservation, Nez Perce Tribe, and Yakama Nation) and other people in the Columbia River Basin. These Tribes are also referred to as Columbia River Treaty Tribes. The first phase of this study was completed in October of 1994 by the Columbia River Inter-Tribal Fish Commission (CRITFC).

This current phase of the study (referred to as Phase II), consisted of evaluating tissue contaminant data representing resident and anadromous fish species that are typically caught by Tribal fisheries in the Columbia River Basin and consumed by Tribal members and other residents of the area. The following Quality Assurance Project Plans (QAPPs) **(1,2)** were used as the overall planning documents for Phase II of the study:

- USEPA Region 10, 1996. Quality Assurance Project Plan, Assessment of Chemical Contaminants In Fish Consumed By Four Native American Tribes In The Columbia River Basin. Revision 6.0. Office of Environmental Assessment, 1200 Sixth Ave., Seattle, WA 90101. December 16.

- USEPA Region 10, 1997. Radionuclide Measurements For Quality Assurance Project Plan, Assessment of Chemical Contaminants In Fish Consumed By Four Native American Tribes In The Columbia River Basin. Revision 2.0. Office of Environmental Assessment, 1200 Sixth Ave., Seattle, WA 90101. September 3.

Information from both phases of this exposure study will be used to assess the potential health impacts to people in the Columbia River Basin from consuming chemical contaminants in Columbia River fish.

Several studies have shown that polychlorinated dibenzo-p-dioxins and polychlorinated dibenzo-p-furans (PCDDs/PCDFs) are present in aquatic biota of several areas of the Columbia River Basin. Studies in the Columbia River Basin have also shown that there are other contaminants of concern in aquatic biota and sediments, including polychlorinated biphenyls (PCBs), and chlorinated pesticides, and inorganics.

The fishery resource in the Columbia River Basin is not only a major food source for Tribal members but it is also an integral part of the Tribes' cultural, economic, and spiritual well-being. Because fish are consumed for both subsistence and ceremonial purposes, there has been concern that Tribal members may be exposed to contaminants in fish because they consume large amounts of fish and eat fish body parts (e.g., fish eggs) that tend to accumulate fat-soluble toxic residues, like PCDDs/PCDFs, PCBs, and chlorinated pesticides.

Because of the levels of contaminants in the Columbia River Basin and because of the importance of fish to the Tribes in the Basin, the U.S. EPA initiated a two-phase exposure study to examine the role of fish consumption as an exposure route for waterborne contaminants among individuals of four Columbia River Basin Tribes.

In Phase I of this exposure study, the U.S. EPA entered into a Cooperative Agreement with the CRITFC in 1990 to formally conduct a fish consumption survey of the four Tribes represented by CRITFC - Confederated Tribes of the Umatilla Indian Reservation, Confederated Tribes of the Warms Springs Reservation, Nez Perce Tribe, and Yakama Nation). This consumption study, published by CRITFC in October of 1994 **(4)**, documented the types and amounts of fish eaten by Tribal members as well as the fish parts consumed and food preparation methods used. The average fish consumption rate of adult Tribal members (combining both fish consumers and non-fish consumers) was 58.7 grams per day. This value is about 9 times higher than the national average fish consumption rate (6.5 grams per day) used by the EPA. The 95th percentile of consumption for adult Tribal members (combining both fish consumers and non-fish consumers) was approximately 170 grams per day. The locations and frequency of use of Tribal fishing sites in the Columbia River Basin, which is the source of about 90% of the fish consumed by Tribal members, were also documented in the survey.

Phase II of this exposure study used the information from the consumption study and from existing data on the levels of contaminants in Columbia River fish to design and implement a sampling program to collect tissue contaminant data from resident and anadromous fish species consumed by Tribal members **(1,2)**. Data from the first (fish consumption survey) and second (tissue contaminant data) phases of this exposure study provide information that can be used to estimate the potential health impacts from consumption of Columbia River fish for these four Tribes and for other consumers of Columbia River Basin fish.

# Chapter 2.0 PROJECT ORGANIZATION

| | |
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| EPA Project Manager | Pat Cirone |
| CRITFC Project Manager (1996-1999)<br>(1999-2000) | Anne Watanabe<br>Paul Lumley |
| EPA Project Leader and Risk Assessor | Dana Davoli |
| EPA Toxicologist/Risk Assessor for Pesticide Measurements | Mike Watson |
| EPA Field Operations Manager | Dave Terpening |
| EPA Sample Collectors and Field Support | Robert Athmann<br>Tom Davis<br>Andy Hess<br>Duane Karna<br>Andy Osterhaus<br>Doc Thompson<br>Philip Wong |
| EPA Administrative Manager | Mary Moore |
| EPA Project QA Manager | Robert Melton |
| EPA Project Manager For Radionuclide Measurements | Richard Poeton |
| EPA Project Statistician | Kris Ryding |
| EPA Regional Laboratory Director | Michael Johnston |
| EPA Regional Laboratory Project Manager | Peggy Knight |
| EPA Regional Laboratory Staff | |
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| Chlorinated Pesticide Measurements | Bob Rieck |
| GIS Compilation and Data Management | Matt Gubitosa<br>Don Matheny |
| EVS Project Manager | Steve Ellis |
| CRITFC Environmental Consultant (1996 - 1998) | Gregory Glass |

The managerial organization of the project is shown in Figure 1. Please note several hundred people provided work and assistance to the project. A more extensive list of contributors to the project are listed in the acknowledgement section of this QA Report. Key project managers had the following assigned responsibilities:

- **EPA Project Manager: Pat Cirone**

  USEPA, Region 10
  (206) 553-1597
  fax: (206) 553-0119

  Pat Cirone was responsible for the overall quality of data and project activities for EPA Region 10. As EPA Project Manager, she worked closely with the CRITFC Project Manager to coordinate all activities of the project. The EPA Project Manager was responsible for ensuring that Region 10 project staff clearly understood their responsibilities and authority on the project. The EPA Project Manager consulted with the Project Leader and approved all deviations from the QAPP.

  The EPA Project Manager reviewed all audit reports and ensured that corrective actions or non-conformances were taken in a timely and appropriate manner. The Project Manager was responsible for ensuring that the QAPP was adequately reviewed prior to implementation of the project.

  Pat Cirone was also the Work Assignment Manager (WAM) for the contract with Tetra Tech/Redmond. As the Work Assignment Manager for TetraTech, she was responsible for ensuring that Tetra Tech and all subcontractors of TetraTech such as EVS Environmental Consultants, implemented the specifications and requirements of the QAPP. Tetra Tech's role in the project was to carry out the requirements of the Work Assignment which was issued and managed by Pat Cirone. In this Report, work completed for EPA Region 10 by the subcontractor, Tetra Tech and EVS, is referred to as work completed by Tetra Tech/EVS.

Insert Figure 1

Figure 1. Project Organization

- **CRITFC Project Managers: Anne Watanabe, Babtist Paul Lumley III, and Sean Darcy**

CRITFC
729 NE Oregon St., Suite 200
Portland, OR 97232
(503) 731-1252
fax: (503) 235-4228

As discussed above, a Cooperative Agreement was developed between CRITFC and U.S. EPA, Region 10, which sets forth the relationship and nature of cooperation between CRITFC and EPA in all aspects of the Phase II study. The CRITFC Project Managers were responsible for coordinating Tribal project activities and to represent the Tribes in communications with EPA. The CRITFC project managers worked closely with the EPA Project Manager to coordinate all activities of the project.

- **EPA Project Leader and EPA Project Risk Assessor: Dana Davoli**

USEPA, Region 10
(206) 553-2135
fax: (206) 553-0119

The EPA Project Leader reported directly to the Region 10 Project Manager. All other Regional Project staff reported directly to the Regional Project Leader. The Regional Project Leader was responsible to the Regional Project Manager for implementing and carrying out the requirements of the QAPP for Region 10. All information concerning project activities was transmitted by Region 10 staff through the Regional Project Leader to the Regional Project Manager. Dana Davoli was also responsible for risk assessment activities for the project.

- **EPA Toxicologist/Risk Assessor for Pesticide Measurements: Mike Watson**

USEPA, Region 10
(206) 553-1072
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Mike Watson was responsible for determining the biological and toxicological significance of project data. This included the examination of the prevalence and trends of chemical residues detected in project samples as they relate to 1) fish species ( tissue, sex, age, etc.), 2) water bodies, sampling locations, and seasons, and 3) the likely significance to human health and environment. Mike Watson was also responsible for a detailed examination of the extent and probable toxicological /biological significance of contaminanants in CRITFC fish species, versus comparable baseline data already established in the available literature for these same species.

! **Field Operations Manager: David Terpening**

USEPA, Region 10
(206) 553-6905
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The Field Operations Manager was responsible for planning and implementing field activities, including fish collection, fish filleting and egg collection, and shipment of samples to the contract lab. In order to carry-out these responsibilities, the Field Operations Manager supervised the EPA sample collectors and field support staff and communicated frequently and periodically with the Regional Project Leader and the Project Manager concerning field activities. The Field Operations Manager reported to the Project Leader.

! **EPA Project Statistician: Kris Ryding**

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Kris Ryding was responsible to graphically represent project data in trend charts and to statistically compare project results.

! **EPA Project Administrative Manager: Mary Moore**

USEPA, Region 10
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The Project Administrative Manager was responsible for tracking and accounting for project costs and assisting project members in obtaining resources for project activities.

! **Regional Laboratory Project Coordinator: Peggy Knight**

USEPA, Region 10
(360) 871-8713
fax: (360) 871-8747

The Regional Laboratory Project Coordinator was responsible for coordination and oversight of the EPA Region 10 Laboratory's work on the Project. Peggy Knight monitored laboratory activities and coordinated communications of laboratory activities and laboratory reports to the Regional Project Leader. The Regional Laboratory Coordinator reported to the Project Leader.

! **Project QA Manager: Robert G. Melton**

USEPA, Region 10
(206) 553-2147
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The Project QA Manager was responsible for implementation of all QA requirements of the QAPP. He was the primary data quality reviewer and validator of the analytical results (PCDD/PCDF congeners and dioxin-like PCBs) from AXYS Laboratory. He oversaw laboratory performance and quality control requirements of the QAPP. The Project QA Manager was responsible for documenting to the Project Leader and Project Manager corrective actions that were implemented. The Project QA Manager reviewed and approved the QAPP before the QAPP was implemented. The Project QA Manager reported on routine project matters to the Project Leader. He was responsible for creating the project chemical database which contains validated chemical measurement results. The Project QA Manager was also responsible for conducting the data assessment of validated project measurement results and for writing the QA Volume for the Project Final Report.

! **EPA Project Manager For Radionuclide Measurements: Richard Poeton**

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(206) 553-8633

The Project Manager For Radionuclide Measurements, Richard Poeton, was responsible for the overall quality of radionuclide data, procurement of radionuclide measurements, validating radionuclide data prior to placement in the project database, conducting the risk assessment of radionuclide expoure, and writing the Radionuclide Summary Volume the the Project Final Report.

! **TetraTech/EVS Project Manager: Steve Ellis**

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! **Tribal Fisheries Program Managers**

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| Yakama Nation | Lynn Hatcher<br>(503) 865-6262 |
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| Confederated Tribes of the Umatilla Indian Reservation | Gary James<br>(541) 276-4109 |
| Confederated Tribes of the Warm Springs Reservation | Patty O'Toole<br>(541) 553-3232 |

! **Tribal Project Leaders**

| | |
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| Risk Assessment, Yakama Nation | Barbara Harper<br>(509) 946-0101 |
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| Manager, Water Resources Division, Nez Perce Tribe | Rick Eichsteadt<br>(208) 843-7370 |
| Manager, Fisheries Division, Nez Perce Tribe | Nancy Hoefs<br>(208) 476-4920 |
| Risk Assessment, Confederated Tribes of the Umatilla Indian Reservation | Stuart Harris<br>(541) 278-5211 |
| Manager, Water Resources Division, Nez Perce Tribe | Patti Howard<br>(208) 843-7370 |
| Manager, Department of Water Resources, Confederated Tribes of the Umatilla Indian Reservation | Stuart Harris |

Steve Ellis was responsible to TetraTech and later to EVS for procuring sub-contracted fish grinding and PCDD/PCDF and PCB congener measurements, and for completing under work assignment orders from EPA a portion of the project final report which documented the results of the study.

# Chapter 3.0 PROJECT SCOPE AND OBJECTIVES

## 3.1 Survey Objectives

Phase II was designed and implemented by EPA with input from representatives of CRITFC and its four member Tribes, the U.S. Fish and Wildlife Service, and the Washington and Oregon State health and environmental agencies.

Prior to the development of the project QAPP **(1,2)**, a preliminary scoping document **(5)** was prepared for EPA by Tetra Tech, an EPA contractor, using data from: (a) the CRITFC fish consumption study; (b) personal communications with Tribal fishery managers and Tribal fishers; and, (c) a data base compiled by Tetra Tech which summarized existing contaminant data on aquatic biota in the Columbia River Basin. This scoping document included a discussion of study objectives and a preliminary study design. At a design conference held in Portland, Oregon, on October 19-20, 1994, and attended by representatives of the organizations listed above, changes to the preliminary scoping document were recommended. The final scoping document, Assessment of Chemical Contaminants in Fish Consumed by Four Native American Tribes in the Columbia River Basin - Final Draft Study Design, was completed on December 2, 1994 **(6)** (subsequently referred to as "draft study design document").

The objectives for Phase II, as discussed in the draft study design document, were two-fold:

1. Measure fish contaminant levels for species and fishing locations being utilized by CRITFC member Tribes to provide, in conjunction with the CRITFC fish consumption report, an assessment of fish consumption among individuals of the Columbia River Basin and these Tribes as an exposure route to residues of toxic waterborne chemicals.

2. Use the information derived from the exposure assessment to estimate potential health risks to fish consumers in the Columbia River Basin. Tribal staff will evaluate exposure and risks to members of their individual Tribes.

This volume of the Final Report will address Objective 1, above. Conclusions regarding potential health risks to fish consumers (Objective 2, above) are presented in other volumes of the Final Report.

The discussion surrounding these two objectives is discussed in more detail in the draft study design document.

## 3.2 Purpose and Scope of QAPP

The project QAPP **(1,2)** provides technical and procedural guidance and requirements to ensure that a well-planned scientific investigation was conducted, and that the field measurements and analytical data obtained serve the project objectives described above. A flow-diagram of project tasks is presented in Figure 2. The content and structure of the QAPP **(1,2)** was based upon requirements and guidelines in Quality Management Program Plan For Region 10, EPA Region 10, Seattle, WA, RQMP-001/92, January 23, 1993, which requires the use of Interim Guidelines and Specifications For Preparing Quality Assurance Project Plans, QAMS-005/80, December 29, 1980, for the preparation of QAPPs involving sampling and analysis projects in EPA Region 10. Specifications for project data quality are presented in Chapter 5 of this report.

Communication has been extremely important for this project because of the number of different organizations and individuals involved as shown in Figure 1 and in Chapter 2.0. Monthly project conference calls were conducted between EPA and CRITFC members to discuss project activities and coordinate project assignments. The Project Manager at EPA Region 10 in Seattle, Washington, was also the Work Assignment Manager (WAM) for the EPA Contractor, Tetra Tech/EVS.

The EPA Field Operations Manager coordinated the field crew of EPA and Tribal staff to collect fish samples. Fish samples which were analyzed as whole fish were sent to a laboratory which was a subcontractor to the EPA Contractor, Tetra Tech/EVS. For those fish in which fillets and/or eggs were collected, fish were first filleted and the eggs collected by the EPA and other field crew members and these fillets and eggs were then sent to the subcontract laboratory, AXYS Laboratory in Sidney, BC, Canada. AXYS Laboratory was responsible for homogenizing all of the fish and egg samples and for preparing sample aliquots for all analyses. AXYS Laboratory also measured fish and egg samples for chlorinated dioxins and furans and dioxin-like PCBs (often referred to as coplanar PCBs). In addition, AXYS Laboratory also sent samples of homogenized fish tissue to the EPA Region 10 Laboratory for analysis (pesticides/Aroclors, semivolatiles including polyaromatic hydrocarbons, and inorganics) and for archiving. A subset of these archived samples was sent to the EPA Montgomery, Alabama Laboratory for all radionuclide measurements except for Technetium measurements which were made by Barringer Laboratory in Golden, Colorado. The Technetium measurements were originally scheduled for completion by the Washington State Department of Health Laboratory in Seattle, Washington. This Seattle laboratory was unable to complete these measurements. Therefore, project samples were subsequently sent to Barringer Laboratory in Golden, Colorado, for Technetium measurements.

Data quality assessment of analytical data was performed by the EPA Project QA Manager. Analytical reports and documentation of dioxin-like PCB measurements and chlorinated dioxin and furan measurements were sent by AXYS Laboratory to the Contractor, Tetra Tech/EVS, and Tetra Tech/EVS transmitted the analytical data to the EPA Project QA Manager for data validation. Validation of data from the EPA Region 10 Laboratory (pesticides/PCBs, semi-volatiles and inorganics) was conducted by the Region 10 Laboratory. The EPA Project QA Manager performed a data quality review of these validation reports. Radionuclide data were validated by the EPA Project Manager for Radionuclide Measurements, Richard Poeton. All validated data were entered into a project chemical database by the EPA Project QA Manager.

The QAPP **(1,2)** provided detailed specifications for field sampling, filleting and homogenization of fish, and chemical analyses. In addition, protocols for documentation, labeling, handling, chain of custody, storage and shipping, and analytical QA procedures were also specified.

A Cooperative Agreement was developed between CRITFC and U.S. EPA, Region 10. The purpose of this Agreement was to set forth the relationship and nature of cooperation between CRITFC and EPA in all aspects of the Phase II study including, but not limited to, sample collection, tissue analysis, data assessment, and data release. The work done in the QAPP **(1)** was completed in cooperation with CRITFC as written in the Cooperative Agreement.

A schedule of sampling activities for the project was proposed in the QAPP **(1)**. A Sample Alteration Form (see Attachment 17 of QAPP **(1)**) was prepared and approved when the sampling schedule required modification.

Insert Figure 2

**Figure 2. Flow Diagram Of Project Tasks**

# Chapter 4.0 FIELD SAMPLING ACTIVITIES

Section 4.0 of the QAPP **(1)** specified planned station locations (Section 4.1), target species and sample types (Section 4.2), sampling strategy (Section 4.3), field collection methods (Section 4.4), and handling of samples and documentation in the field (Section 4.5). Actual project sampling locations and collection specifications are listed in Appendix A, Tables A-1 and A-2 of this Report. A list of samples which were measured for radionuclides is provided in Appendix A, Table A-1.

All of the field sampling for the project was coordinated by both EPA Region 10 and CRITFC Tribal members. Field sampling required either adherence to the following specifications in the QAPP **(1)** or modification to the QAPP as approved by the Field Operations Manager :

- The collection of field samples which are representative of the fish consumed by Tribal members as described in Phase I of the study,
- The responsibilities of each member of the field team,
- Study objectives and time commitments for this project,
- Collection permit requirements,
- Site locations and collection equipment and gear needed at each site,
- Proposed sampling dates and species of interest for each site location,
- Composite sample size for each species and sample type, and
- Fish handling procedures and storage requirements.

## 4.1 Station Locations

The CRITFC fish consumption survey (4) identified 102 fishing sites used by the four Tribes in the Columbia River Basin. Due to resource constraints, all of these sites could not be sampled in Phase II of EPA's exposure study. The draft study design document referred to in Section 1.2 of the QAPP **(1)** discusses in detail the process that was used to reduce the number of sites to be sampled to 13 sites. Initially, in the QAPP **(1)**, fishing sites that represented greater than 40 percent of each Tribe's fishing use for resident and anadromous fish species were identified. This number of fishing sites (24 sites) was reduced to 8 sites by

3. Selecting one site at the base of a watershed to represent the entire watershed for the Deschutes (site 98), Clearwater (site 96), and Umatilla (site 30) Rivers, and,

4. Limiting the number of sites on the mainstem Columbia River to be sampled to sites 6, 7, 8, 9 and 18.

Additional sites were added to the QAPP because they were near local pollution sources of concern to the Tribes (sites 48 and 49 on the Yakima River, and site 79 on the Salmon River); contained species of special concern to the Tribe such as smelt (site 57 on the Cowlitz River); or provide needed geographical coverage (site 21 on the Willamette River). Use of this decision tree in the QAPP resulted in the selection of a total of 13 sites for sampling (see Figure 3).

Subsequent to the completion of the draft study design document, additional discussions were held with CRITFC Tribal fisheries program managers and Tribal staff. In these discussions, it was decided that for sites 9, 18, and 21, it was easier to collect samples of salmon from nearby salmon hatcheries that supply salmon to the Tribes. This was because recent data on fish runs suggested that low numbers of salmon may return to sites 9, 18, and 21. Also, using the fish returning to the hatcheries helped reduce some of the field collection time and sampling effort for this project. Therefore, at site 21, no salmon were caught. Instead, salmon were taken at site 21B (Dexter Hatchery on the McKenzie River). Salmon that were to be caught at site 9 were taken at site 14 (Priest Rapids Hatchery on the Columbia River); and, salmon that were scheduled to be caught at site 18 were taken at site 51 (Icicle Hatchery on the Wenatchee River). Other species were caught as planned at sites 9, 18, and 21. An updated decision tree was placed in the QAPP **(1)** and included 16 sites. It should be noted that site 14 provided information on a local pollution source of concern, while sites 21 and 51 provided the geographical coverage used in the decision tree.

The map of sampling locations listed in Figure 4 are the original sampling sites specified in the QAPP **(1)**. The fish which were actually collected with revised station numbers are shown in the map in Figure 5.

A Global Positioning System (GPS) was used to mark sampling locations (e.g. latitude and longitude) (see Appendix A, Table A-2) during fish collection efforts and this information was transferred to the map in Figure 5.

## 4.2 Target Species and Sample Type

Appendix A, Tables A-1 and A-2 show the locations, species, and sample types that were collected during the entire 1996-1998 study. The selection of species to be collected was based primarily on consumption data presented in the CRITFC Fish Consumption Report. Input during the design conference in Portland and from the CRITFC Tribal members were also considered. The primary target species, and two additional species (channel catfish and smallmouth bass) which were added when additional resources became available, are listed below:

| | |
|---|---|
| Chinook salmon | **Oncorhynchus tshawytscha** |
| Coho salmon | **Oncorhynchus kisutch** |
| Steelhead trout | **Oncorhynchus mykiss** |
| Rainbow trout | **Oncorhynchus mykiss** |
| Mountain whitefish | **Prosopium williamsoni** |

| | |
|---|---|
| Lake whitefish | **Coregonus clupeaformis** |
| White sturgeon | **Acipenser transmontanus** |
| Walleye | **Stizostedion vitreum** |
| Largescale sucker | **Catostomus macrocheilus** |
| Bridgelip sucker | **Catostomus columbianus** |
| Pacific lamprey | **Lampetra tridentata** |
| Eulachon (smelt) | **Thaleichthys pacificus** |
| Channel catfish | **Ictalurus punctatus** |
| Smallmouth bass | **Micropterus dolomieu** |

It should be noted that although lake whitefish were targeted for collection in the QAPP **(1)**, these fish were not present in the various habitats chosen for field collection.

Table 1 shows the fish species that are consumed by Tribal members and the fishing sites where fish are collected. Tissue samples for all consumed species except northern pikeminnow (previously called northern squawfish) (*Ptychocheilus oregonensis*) and American shad (*Alosa sapidissima*) were collected. These two species are consumed by only a small fraction (<2.7 percent) of adult Tribal members **(4)**.

Four types of samples were collected: whole-body (WB), fillet with skin (FS), fillet without skin (FW), and eggs (E). Whole-body samples were selected for several species to maximize the chances of measuring detectable levels of contaminants of concern and because data presented in the CRITFC fish consumption study showed that Tribal members may consume several fish parts in addition to the fillet (Table 2). Eggs from spring chinook salmon, fall chinook salmon, and steelhead were measured because consumption data show that salmonid eggs are widely consumed by Tribal members (Table 2). Because of the high lipid levels in eggs, concentrations of hydrophobic organic chemicals may reach substantially higher levels than in other fish tissues. Salmonid heads were not designated as a matrix for compositing and analysis due to limited project resources and because the CRITFC fish consumption study did not indicate that most Tribal members consumed large amounts of Salmonid heads on a frequent basis. However, heads did constitute a portion of the measurement of whole body samples.

Contaminant levels in various fish parts (i.e., whole-body, fillet, and eggs) were measured so that this information can be used to provide guidance on how to prepare fish, or what parts should be avoided, in the event that contaminant levels exceed levels that warrant concern. In addition, the conversion factors developed from these data (e.g., whole-body-fillet and whole-body-egg ratios) may assist in the comparison of the data from this study with other historical data that exist from the Columbia River Basin.

### 4.3 Sampling Strategy

The sampling strategy used for this study is consistent with guidance provided in the document entitled: **Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories, Volume I: Fish Sampling and Analysis (7)**. For most fish species except white sturgeon, three replicate composite samples were measured from each collection site. At some sites (see Appendix A, Tables A-1 and A-2), samplers were unable to collect enough fish in order to create three replicate composite samples. For white sturgeon, composite samples were not collected. Instead three individual fish were measured from each collection site. The planned number of fish per composite varied for different species: approximately 100 individuals per composite for smelt, 21 individuals per composite for lamprey, 8 individuals per composite for resident (non-salmonid) species, and 3 to 5 individuals per composite for salmon and steelhead. U.S. EPA (4) recommends that 3 to 10 individuals should be collected for a composite sample for each target species and that the same number of individual organisms should be used to prepare all replicate composite samples for analysis of contaminants for a given target species at a given site. Several fish contaminant studies in the Columbia River Basin used composites of 8 individuals per sample, so the use of a similar number would simplify comparisons with other available data. Because of the small size of lamprey and smelt, a composite of 8 individuals would not provide enough tissue for all chemical analyses, therefore a nominal value of 20 individuals per composite was suggested by the Design Conference attendees for smelt and lamprey, respectively. To ensure adequate sample volume for analyses, EPA, Region 10, decided to increase the composite size for smelt to 100 fish. Design Conference attendees felt that the number of individuals per composite for salmon and steelhead should be reduced from 8 to 5 (some individuals suggested 3) because of concerns about the ability to collect sufficient numbers of fish, and because it was felt that the study should strive to minimize impacts on endangered species.

At the Design Conference, it was also recommended that if possible, all fish used in a composite be female. However, Native Americans eat what they collect (i.e. both males and females). Therefore, the decision was made to collect random samples of fish for each composite rather than all females. The exception to this was at site #8 in September of 1997. At this site at this time, for fall chinook salmon and steelhead, the fish used for the fillet with skin composites were as follow:

Steelhead Composite 1 - random - both male and female (composite number 97380993)
Steelhead Composite 2 - 3 fish, all female (composite number 97380994)
Steelhead Composite 3 - 3 fish, all male (composite number 97380995)

Fall chinook salmon Composite 1 - random - both male and female (composite number 97380987)
Fall chinook salmon Composite 2 - 3 fish, all female (composite number 97380988)
Fall chinook salmon Composite 3 - 3 fish, all male (composite numbers 97380989 and 97380997)

**Figure 3. Decision Tree For Selection of Tissue Sampling Sites**

Insert Figure 4

**Figure 4. Map of Proposed Sampling Locations.**

Insert Figure 5

**Figure 5. Map of Actual Sampling Locations.**

The above sampling scheme for steelhead and fall chinook salmon provided information on the lipid content of males and females of these two species in September of 1997. Actual project lipid measurements for these composites showed that the lipid values in the composites which contained female fish were higher than the lipid values in the composites which contained male fish (see Appendix A, Table A-1).

Collection dates for each species are listed in Appendix A, Tables A-1 and A-2. According to U.S. EPA guidance **(7)**, the collection period should ideally avoid the spawning period of the target species because many fish are subject to stress during spawning. However, because eggs were to be collected from salmonid species and because the CRITFC Tribes frequently fish for salmonids when they are spawning, the typical spawning period for these species were targeted. For resident species, collection periods were proposed so that spawning periods were avoided. For white sturgeon, the proposed collection period was consistent with Tribal fishing seasons.

For each target species composite, a single size class was targeted at the site. Because the concentrations in fish for some pollutants (e.g., PCBs and mercury) have been shown to increase with age and size, an attempt was made to collect a composite that represents the larger fish being caught at the sampling site during the sampling period. Therefore, the selection of fish for the composite, when possible, adhered to the following two criteria:

1. Composites were comprised of fish that were in the upper 75% of fish length of those fish caught by the CRITFC Tribes near the sampling location, and;

2. Composites were collected according to EPA guidance **(7)** which recommends that the smallest individual in a composite be no less than 75% of the total length of the largest individual.

Both replicate composite samples and field duplicate composite samples for a target species were as similar to each other as possible. For this project, replicate samples were in most instances three similar samples of the same species, same type of sample (WB, FS, FW, E), and collected on the same location and same day. For this project, duplicate samples consisted of the opposite fillets (right fillet (F1) *versus* left side fillet (F2)) of the same species, same type of sample (FS, FW), and collected on the same location and same day. For example, all of the FS and FW samples used for project measurements were of the right side fillet (F1), whereas, for those composite samples which were designated as a field duplicate composite samples, these duplicate samples were from the left side fillets (F2) of the same fish. Table A-1 in Appendix A lists which samples were replicate composite samples and which samples were field duplicate samples. Table A-1 in Appendix A designates a Composite Group Number for each set of replicate samples and a Field Duplicate Number for each set of duplicate samples. Table A-1 in Appendix A shows that the project collected 105 sets of replicate samples and 9 sets of field duplicate samples. The relative difference between the average length of individuals within any composite sample and within each set of replicate samples from a given site did not exceed 10 percent in most cases.

**Table 1. Percentage of Adult Tribal Members Consuming Proposed Target Species and Species Collection Sites**

| Species | Weighted Percent Who Consume the Species | Proposed Fishing Sites | |
|---|---|---|---|
| | | Site Numbers | Site Locations (Rivers) |
| Salmon | 92.4% | 8, 9, 14*, 21A*, 30, 51* | Columbia, McKenzie, Umatilla, Wenatchee, |
| Lamprey | 54.2% | 21, 6 | Willamette, Columbia |
| Trout [a] | 70.2% | 98, 8, 18, 30, 48, 49, 96*, 79 | Deschutes, Columbia, Umatilla, Yakima, Clearwater, Salmon |
| Smelt | 52.1% | 57 | Cowlitz |
| Whitefish | 22.8% | 8, 30, 96 | Columbia, Umatilla, Clearwater |
| Sturgeon | 24.8% | 6, 7, 8, 9, 96 | Columbia, Clearwater |
| Walleye | 9.3% | 8 | Columbia |
| Sucker | 7.7% | 98 | Deschutes |
| Squawfish | 2.7% | none | none |
| Shad | 2.6% | none | none |

[a] Rainbow Trout and Steelhead.
* Hatchery Site.

**Table 2. Columbia River Inter-Tribal Fish Commission Exposure Study: Adult Consumption of Fish Parts**

| Species | Parts | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Fillet | | Skin | | Head | | Eggs | | Bones | | Organs | |
| | N | Weighted % Who Consume | N | Weighted % Who Consume | N | Weighted % Who Consume | N | Weighted % Who Consume | N | Weighted % Who Consume | N | Weighted % Who Consume |
| Salmon | 473 | 95.1% | 473 | 55.8% | 473 | 42.7% | 473 | 42.8% | 473 | 12.1% | 470 | 3.7% |
| Lamprey | 249 | 86.4% | 251 | 89.3% | 250 | 18.1% | 250 | 4.6% | 250 | 5.2% | 250 | 3.2% |
| Trout | 365 | 89.4% | 365 | 68.5% | 365 | 13.7% | 364 | 8.7% | 365 | 7.1% | 362 | 2.3% |
| Smelt | 209 | 78.8% | 209 | 88.9% | 210 | 37.4% | 209 | 46.4% | 210 | 28.4% | 206 | 27.9% |
| Whitefish | 125 | 93.8% | 124 | 53.8% | 125 | 15.4% | 125 | 20.6% | 125 | 6.0% | 124 | 0.0% |
| Sturgeon | 121 | 94.6% | 121 | 18.2% | 121 | 6.2% | 121 | 11.9% | 121 | 2.6% | 121 | 0.3% |
| Walleye | 46 | 100% | 46 | 20.7% | 46 | 6.2% | 46 | 9.8% | 46 | 2.4% | 46 | 0.9% |
| Sucker | 15 | 89.7% | 15 | 34.1% | 15 | 8.1% | 15 | 11.1% | 15 | 5.9% | 15 | 0.0% |
| Squawfish | 42 | 89.3% | 42 | 50.0% | 42 | 19.4% | 42 | 30.4% | 42 | 9.8% | 42 | 2.1% |
| Shad | 16 | 93.5% | 16 | 15.7% | 16 | 0.0% | 16 | 0.0% | 16 | 3.3% | 15 | 0.0% |

Source: CRITFC (1).

The following types of samples were selected for radionuclide analysis in the addendum to the QAPP **(2)**:

| | |
|---|---|
| Site 7: | sturgeon fillet without skin (3 replicates) |
| Site 8: | sturgeon fillet without skin (3 replicates)<br>sturgeon whole (3 replicates)<br>whitefish fillet (3 replicates)<br>whitefish whole (3 replicates) |
| Site 9: | sturgeon fillet without skin (3 replicates)<br>whitefish fillet (3 replicates)<br>whitefish whole (3 replicates)<br>other fillet (catfish or sucker) (3 replicates)<br>other whole (catfish or sucker) (3 replicates) |
| K Pond:<br>(see Table A-1) | sturgeon fillet without skin (3 replicates)<br>sturgeon whole (3 replicates) |

Laboratory duplicates: 2

In addition, the following samples from an upstream location (Site 96) were selected:

sturgeon fillet without skin (3 replicates)
whitefish fillet (3 replicates)
whitefish whole (3 replicates)

Appendix A, Table A-1 specifies the actual location of the 45 samples which were measured for radionuclides.

### 4.4 Field Collection Methods

Sampling methods for fish included: electrofishing, hand collection, hatchery collection, trapping at dams, dip netting, fish traps, and gill netting. The preferred method was dependent on the conditions at the sampling site, selected species, and legal constraints. Collection of fish by all methods were controlled by stipulations of the federal, state and Tribal requirements.

#### 4.4.1 Electrofishing

Electrofishing was considered to be the most efficient method for collecting a variety of species in large rivers because it is easily standardized and less selective than alternative gear. However, electrofishing was generally not effective in capturing fish that were at depths greater than about 10 feet, therefore alternative methods, such as gill netting, were used for some species. In this project the boat mounted electro shocker was used in deeper rivers. At some locations on smaller

rivers (i.e., Upper Umatilla and Upper Klickitat Rivers) water depths were not sufficiently deep to use the boat for electrofishing. In these shallow locations, sampling was done using electro backpack shocking equipment allowing for the selection of the fish species of interest (see Appendix A, Table A-2). Rainbow trout, whitefish, walleye, and sucker from selected locations (as shown in Appendix A, Table A-2) were captured by electrofishing.

### 4.4.2 Gill Netting

Gill nets capture fish by entanglement. They are particularly well-suited for the capture of highly mobile fish (e.g., salmonids and some selected sturgeon) which are not easily captured by electrofishing. For this project, sinking gill nets (approximately 100 ft long by 6 ft or 12 ft deep) and surface gill nets were used, each of which consisted of variable mesh (2 to 6 inch diameter) monofilament line attached to cork and lead lines. The nets were anchored with lead mushroom weights and marked with the appropriate information identifying who the nets belong to and how they were being used (i.e., research). Floats and buoys were used to help mark net deployment areas.

Gill nets were deployed for both day and night operations and monitored during fishing efforts. After several hours, nets were retrieved and the captured fish collected. All non-target fish species and all targeted fish species that were not within the desired size category were returned to the water, whether dead or alive. A field record was kept of fish that were taken for each gill net set.

### 4.4.3 Traps at Selected Dams

At selected barrier dams on the Hood River, Umatilla River, the Yakima River, and Willamette Falls, some fish were collected using traps behind weirs. Samples of selected fish species (e.g., steelhead, salmon, and lamprey) were taken from weirs using either elevator lifts or dip nets.

### 4.4.4 Set Traps

At selected locations on the Yakima River, some catfish were collected using traps in shallow, slow-moving areas of the river.

### 4.4.5 Dip Nets

Dip nets were used in some selected areas where fish were migrating, such as smelt, steelhead, salmon, and lamprey, following the shoreline of the river. Dip nets are usually made with small mesh (e.g. ½" to 3") and used to dip up fish in small confined areas such as shallow pools, rapids, or waterfalls. Sampling nets were monitored at all times. Once a fish was caught, the dip net was pulled to the surface and the fish removed. Only fish selected for the project were retained and other species were released.

### 4.4.6 Hatchery

Specific fish returning to selected hatcheries were targeted for collection and retrieved from holding ponds. This type of sampling was coordinated with hatchery management personnel so

that the fish were taken from holding pond areas before their eggs and sperm were removed and before any type of chemical treatment had been applied.

### 4.4.7 Hand Collection

The hand collection method of sampling was used in and around the Willamette Falls at the fish ladder and Fifteen Mile Creek for lamprey. As the lamprey migrated over the falls area, they were collected off the rocks, fish ladder, and from shallow pools with small nets, snag-poles, or by hand.

### 4.4.8 Set Lines

Set lines were used to collect sturgeon from selected locations on the Columbia River. Six hundred foot set lines were anchored, marked with buoys and/or floats, and baited approximately every 20 feet. Lines were monitored day and night. When the set line was pulled to the surface and fish removed, non-targeted fish were released.

## 4.5 Fish Sample Handling in the Field

### 4.5.1 Sample Integrity

The EPA Field Operations Manager was present at all times when fish were collected in order to assure sample integrity.

Sample integrity required that fish be handled in a manner that minimized loss of contaminants in fish and prevented extraneous tissue contamination. Sources of extraneous tissue contamination include contamination from dirty hands, sampling gear, greasy cables, spilled engine fuel, engine exhaust, dust, ice chests, and ice used for cooling. Loss of contaminants in fish tissue were controlled in the field by selecting fish specimens that had a minimum amount of skin lacerations.

The following field sampling procedures were used to collect project samples:

- Caught fish were only placed on clean surfaces, such as aluminum foil.
- Ice chests were cleaned prior to any sampling activities.
- Samples were placed in waterproof plastic bags to avoid contamination from melting ice.
- All utensils or equipment used directly in handling fish ( e.g., fish hooks, measuring boards and fish clubs) were cleaned in the laboratory or field with ambient water prior to each field sampling effort and placed in aluminum foil.
- The field collection team cleaned equipment between sampling sites by rinsing with ambient water and re-wrapping equipment in aluminum foil.

### 4.5.2 Handling Of Field Samples During Collection

After retrieval of fish from sampling devices, each fish was identified by species by personnel familiar with the taxonomy of the fish in the Columbia River Basin. The length of collected fish were measured to ensure that they met the size class as defined in the QAPP **(1)**. Based upon size of fish caught in the field, the acceptable size range of fish was determined by the Field Operations Manager and documented using a Sample Alteration Form (see Attachment 17 in the QAPP). Those fish that did not meet the target size class were released. Fish that did meet the target size class were subdued by a sharp blow or blows to the base of the head. All individual fish (with the exception of smelt) that were kept were assigned a unique identification number (EPA Sample #) consisting of an numeric eight digit code XXXXXXXX. Fish were then assigned to one of three composite samples for that location. Numbers were chosen to be consistent with EPA Region 10's sample management tracking system. Selected specimens were photographed. For lamprey and smelt, each fish was placed into one of three composite groups (approximately 20 per composite for lamprey and 100 per composite for smelt) and each composite group was assigned an identification number.

The Field Operations Manager and the EPA field support staff wrapped each whole fish (with the exception of smelt) in clean heavy-duty aluminum foil. The whole fish was then placed into a plastic bag and the bag was tied and labeled. For lamprey the composite group was wrapped in aluminum foil and tied in a plastic bag. For smelt, the composite group was placed in a plastic bag and sealed. The Field Operations Manager and EPA field support staff immediately packed bagged fish samples on ice in clean ice chests to start cooling of fish. These cooled samples were placed on dry ice as soon as possible.

### 4.5.3 Documentation During Fish Collection

The Field Operations Manager was personally responsible for the care and custody of fish samples until they were properly transferred or dispatched to the storage and/or filleting facility or to AXYS Laboratory. He also determined if custody procedures were followed properly during the field work and if additional samples were required.

Documentation for fish collection was made in the following documents: 1) on the Field Record Form; 2) in the Sampler's Notebook; 3) on the Sample Identification/Chain of Custody Tag, and 4) on the Chain-of-Custody Form. Volume 3 of the Final Report **(8)** and the Field Operations Manager sampler's notebook(s) provide a record for the collection of project composite samples.

Field Record Form - EPA developed for the project, a standard Field Record Form that was filled out by the EPA Field Operations Manager at each sampling location **(8)**. The information listed below was included on this Field Record Form:

Geographic location (latitude and longitude) using Global Positioning System
Species name
Date and time
Method of collection (e.g., gill net, trap, electrofish, etc.)
Station number
Sample identification number / numbers

Composite sample number
Weather conditions (e.g., cloud cover, rain or shine, windy)
Water depth of capture (feet)
Sex of species
Evidence of hatchery markings (e.g.., fin clips, tags)(under "Comments")
Total fish length (in metric units)
Total fish weight (in metric units to the nearest gram)
Sampling crew names
Type of vessel
External marks or gross physiological abnormalities noted
(under "Comments")

Sampler's Notebook - The sampler's notebook included the same information that was recorded on the Field Record Form. In addition, the Sampler's Notebook documented any unusual activities or problems encountered in the field. It also included a record of any photographs taken in the field.

Sample Identification/Chain of Custody Tag - A waterproof Sample Identification/Chain of Custody Tag (SI/COC Tag) was completed in indelible ink for each individual fish (or composite for lamprey and smelt) and taped or written on each aluminum-foil-wrapped specimen(s) before placing the specimen(s) in a plastic bag in the field. Photo records of each of these sample tags were reproduced in each of the PCDD/PCDF analytical reports which were sent to EPA from AXYS Labs. These tags included the following information: station location/number, sampling date and time, species name, sample type, number of fish in the designated composite, fish sample and/or composite number, and the name and signature of the sampler.

Chain-of Custody Form - A Region 10 Chain-of-Custody Form (COC Form) **(8)** was completed in indelible ink for each shipment that was made. These COC forms were enclosed in plastic and taped to the inside lid of the cooler. The information on this form was used to track all samples from field collection to receipt at AXYS Laboratory to receipt by the EPA Manchester Laboratory, the EPA National Air and Radiation Environmental Laboratory (NAREL) in Montgomery, Alabama, and Berringer Laboratory in Golden, Colorado.

## 4.6 Sample Storage

### 4.6.1 Storage Procedures

As previously specified, once fish were caught, the Field Operations Manager and EPA field support staff immediately packed the bagged fish samples in ice (preferably dry ice) to start cooling the fish. If fish were filleted the same day that they were caught or if they were whole body samples or egg samples, they were immediately packed in dry ice and frozen. Fish that were not filleted the day they were caught were packed on ice and transported to the EPA Laboratory or to another prearranged locations (e.g. local fish hatcheries) where they were filleted and then frozen at a temperature $\leq$-20 $^{o}$C. Chain of custody procedures were used for all phases of sample processing and shipment.

### 4.6.2 Documentation

The COC Forms and SI/COC Tags were kept with stored samples until samples were removed for filleting and/or shipping.

## 4.7 Filleting of Fish

The Field Operations Manager or EPA field support staff (with oversight by the Field Operations Manager) filleted all selected fish samples. The samples which were filleted are identified in Appendix A, Tables A-1 and A-2. Filleting was done at the EPA Laboratory or at a field laboratory that permitted appropriate quality control procedures (e.g., a fish hatchery or EPA's mobile trailer.)

### 4.7.1 Filleting Procedures

Fish were handled following the guidance provided in sections 7.2.1 (General Considerations) and 7.2.1.3 (Samples for Both Organics and Metals Analyses) in **(7)**. If rupture of organs was observed for an individual fish, the specimen was eliminated from the composite sample. For scaling and filleting, the methods described in sections 7.2.2.6 and 7.2.2.7 and illustrated in Figure 7-3 of **(7)** were followed.

As is described is Sections 4.3, 5.2.1, and 8.2, precision of project samples were measured by collectiong both replicate composite samples and field duplicate composite samples for target species were as similar to each other as possible. For this project, replicate samples were in most instances three similar samples of the same species, same type of sample (WB, FS, FW, E), and collected on the same location and same day. Duplicate field samples consisted of the opposite fillets (right fillet (F1) *versus* left side fillet (F2)) of the same species, same type of sample (FS, FW), and collected on the same location and same day. For example, all of the FS and FW samples used for project measurements were of the right side fillet (F1), whereas, for those composite samples which were designated as a field duplicate composite samples, these duplicate samples were from the left side fillets (F2) of the same fish. The Field Operations Manager created composites of fillets (with and without skin) using the fillet from the right side of each fish (the “F1") (right side to be determined from the perspective of the direction in which the fish would swim). This composite was wrapped in clean aluminum foil and placed in a plastic bag. The Field Operations Manager wrapped the left side fillet from each fish separately in heavy duty aluminum foil and added the two digit identifier “F2" to the sample tag, field sampler’s notebook, and field data sheet. The individual fillets (the "F2"s) that were not ground and composited were placed in individual plastic bags with the composite identification number, the individual identification numbers, and the date of resection. The Field Operations Manager shipped these F2 samples to the EPA Region 10 laboratory for storage.

### 4.7.2 Documentation Procedures During Filleting

Documentation for fish filleting consisted of recording information in the following documents **(8)**: 1) on a Sample Processing Record; 2) in the Field Operations Manager's Field Samplers' Notebook; and 3) on the Sample Identification/Chain of Custody Tag.

#### 4.7.2.1 Sample Processing Record

Sample processing records were kept for each individual sample, composite of whole fish, fillets and eggs. Records included the following information:

- Information on sample type and species name
- Unique sample number for individual fish and/or fish (egg) composite number (identical to that number assigned during sampling)
- Weights of unprocessed individual fillets and egg skeins

#### 4.7.2.2 Filleter's Notebook

In addition to the information described above, the filleter (the Field Operations Manager or Region 10 designee) recorded the following information in a Field Sampler's Notebook and Field Sample Data Sheet:

- Evidence of hatchery markings on fish (e.g., fin clips and tags) in addition to those noted in the field,
- Incidence of external abnormalities (e.g., fin erosion, skin ulcers, skeletal anomalies, tumors) in addition to those noted during field sampling,
- Incidence of internal abnormalities, if any, and
- Record of scales and/or pectoral fins collected.

Scales for age determination were collected from selected fish such as salmonids. Scales were placed in small jars and preserved with ethanol. For sturgeon, one pectoral fin was removed by EPA prior to filleting for future age determinations. Pectoral fins were placed in plastic bags and frozen. Each scale or fin sample taken was given a matching EPA sample number.

#### 4.7.2.3 Sample Identification/Chain-of-Custody Tag

After filleting, SI/COC Tags (containing the information described in section 4.5.3) were attached to the aluminum foil on samples. These were then be placed in plastic bags and frozen.

## 4.8 Shipment of Samples and Receipt by Subcontract Laboratory

In preparation for shipping, the Field Operations Manager packed frozen whole fish, fillets, and egg samples securely inside coolers. Each cooler was sealed with glass fiber tape and a custody seal (shown in Attachment 10 of the QAPP **(1)**) was attached so that it must be broken in order for the cooler to be opened. All fish samples were packaged and shipped frozen via Horizon Airlines to AXYS Laboratory for further processing. All coolers were received at AXYS Laboratory within 12 hours of shipment from EPA Manchester Laboratory. These same procedures were followed by AXYS Laboratory when processed samples were sent back to the EPA laboratory for analysis and archiving.

The EPA Field Operations Manager notified the Tetra Tech/EVS contact person when each group of project samples were shipped. The Tetra Tech/EVS contact person was given both a hard copy and electronic copy of sample ID numbers, number of ice chests being sent, and species of fish being sent in each shipment. Upon arrival at the laboratory, Tetra Tech/EVS and the project Field Operations Manager were notified that samples had been received in good condition by AXYS Laboratory. When fish tissue was not processed immediately at AXYS, samples were stored in a secure freezer at $\leq$-20$^{o}$ C until they were removed for processing.

### 4.8.1 Documentation Requirements

The original Region 10 Chain-of-Custody Forms were signed by the Field Operations Manager and enclosed in plastic and taped to the inside lid of one cooler of each group of coolers shipped. A custody seal was attached to each cooler so that it must be broken when the cooler was opened. The Sample Processing Records and the SI/COC Tags for each sample were shipped at the same time. In addition, one photocopy of all of the paperwork sent to AXYS Laboratory was sent to the Tetra Tech/EVS contact person via Federal Express or FAX and one copy was retained by the Field Operations Manager. Photo copies of the Chain of Custody Forms, sample Processing Records, and SI/COC Tags were also included in analytical reports from AXYS Laboratory for PCDD/PCDF data reports.

AXYS sent all return delivery receipts to Tetra Tech/EVS. A copy of the Chain-of-Custody Form for each shipment was sent by AXYS Laboratory to the EPA Project Manager within 7 calendar days of receipt of each shipment of samples.

In addition, AXYS Laboratory contacted the Field Operations Manager after the laboratory received each batch of samples to let the Field Operations Manager know that sample integrity was maintained during shipment. The following information was communicated to the Field Operations Manager by telephone or FAX within 24 hours after samples were received by AXYS: (1) condition of the samples upon arrival at the laboratory (e.g. to ensure sample degradation had not occurred during shipment); (2) time delays (e.g., not arriving the next day); and, (3) condition of chain-of-custody seals. A project file including a copy of all Chain of Custody forms, field notebooks, *etc.*, was maintained by the Field Operations Manager at the EPA Region 10 Seattle office.

# Chapter 5.0 PROJECT QUALITY ASSURANCE OBJECTIVES

## 5.1 Project Quality Objectives

Project data quality objectives were established in revision 6.0 of the QAPP **(1)**. The QAPP is a formal EPA project document that specifies the operational procedures and quality assurance/quality control (QA/QC) requirements for obtaining environmental data of sufficient quantity and quality to satisfy project objectives. QAPPs are an important part of the EPA Quality System, and they are required for all data collection activities that generate data for use by EPA. QAPPs contain information on project management, measurement and data acquisition, assessment and oversight, and data validation and useability. Data Quality Objectives (DQOs) are formal elements of a QAPP, yet information contained in the DQOs relate indirectly to many other elements of the QAPP. DQOs provide statements about the expectations and requirements of the data *user* (such as a decision maker). For this project, these requirements were translated into measurement performance specifications and QA/QC procedures for project data *suppliers*, in order to provide them with the information they needed to satisfy the data user's needs.

The overall QA objective for project analytical data was to ensure that data of known and acceptable quality were produced so that potential health risks to fish consumers could be estimated. Data quality objectives (DQOs) for the project are discussed below, in Table 3, in the attachments to the QAPP **(1),** and in other sections of the QAPP. Project DQOs include:

- The selection of the appropriate chemical target compounds to be measured and the appropriate quantitation limits for these compounds, and,

- Analytical objectives as defined by measurement of precision, accuracy, representativeness, completeness, and comparability of quality assurance samples such as field duplicate samples, performance evaluation samples, and laboratory quality control samples. These QA and QC samples were used to evaluate project data to determine if data meet the specified DQOs of the QAPP.

### 5.1.1 Selection of Target Compounds and Detection Limits

As discussed in Section 1.2, the objectives for Phase II were to measure fish contaminant levels for species caught at fishing locations being utilized by CRITFC Tribal members. The selection of target compounds and the risk-based detection limit goals were determined in the draft study design document prepared for this project by Tetra Tech (3) and EPA. In this document, target analytes were selected by considering guidance provided by the U.S. EPA (4) and by performing a health risk-based screening analysis of tissue contaminant data collected within the Columbia River Basin during the last ten years (1984-1994).

## Table 3. Sampling and Measurement Objectives and Requirements For the Project

| Analytical Group | Actual Number of Field Samples[1,6] | Number of QA Samples: PE[2], MS/MSD[2] Field Dups[1] | Matrix | Method | Accuracy[3] | Precision[4] (RPD) | Complete-ness | Preser vation | Containers (Field/Lab) | Holding Time For Project Samples |
|---|---|---|---|---|---|---|---|---|---|---|
| PCDDs/ PCDFs/ % Lipids | 284 | 6 PE's 9 Dups | Fish Tissue | 1613B + Lab SOW | 70 to 140% | 40% | 90% | -20°C | Al foil/ 2x2ozWM | 1 yr. (sample) 40 days (extract) |
| Dioxin-Like, PCBs | 284 | 6 PE's 9 Dups | Fish Tissue | 1668 | 70 to 140% | 40% | 90% | -20°C | Al foil/ 2x2ozWM | 1 yr. (sample) 40 days (extract) |
| Chlorinated Pesticides/ Aroclors | 295 | 12 MS/MSDs 9 Dups | Fish Tissue | 8081 Florisil/Acetonitrile Partitioning/Florisil | 30-150% | 50% | 90% | -20°C | Al foil/ 2x2ozWM | 1 yr. (sample) 40 days (extract) |
| AED/ Pesticides | 85 | 6 MS/MSDs 9 Dups | Fish Tissue | 8085 Acetonitrile Partitioning | 30-150% | 50% | 90% | -20°C | Al foil/ 2x2ozWM | 1 yr. (sample) 40 days (extract) |
| Neutral Semivol. | 295 | 16 MS/MSDs 9 Dups | Fish Tissue | 8270/SIM GPC/SG | 30-140% | 50% | 90% | -20°C | Al foil/ use SV ext | 1 yr. (sample) 40 days (extract) |
| Chlorinated Phenolics | 295 | 15 MS/MSDs 9 Dups | Fish Tissue | 1653 Modified GPC/Acetylation | 20-150% | 50% | 90% | -20°C | Al foil/ 2x2ozWM | 1 yr. (sample) 40 days (extract) |
| Metals | 295 | 16 MS/MSDs 9 Dups | Fish Tissue | 200.3 & 200.8[5] | 60-140% | 30% | 90% | -20°C | Al foil/ 2x2ozWM | 2 yrs. |
| Mercury | 299 | 40 MS/MSDs 9 Dups | Fish Tissue | 251.6[5,] Rev. 2.3 | 60-140% | 35% | 90% | -20°C | Al foil/ use ICP WM | 86 days |
| Radionuclides | 43 | 2 Dups | Fish Tissue | EPA NAREL SOPs | | | | -20°C | 1x1kg WM | none |

[1] - The total number of samples in column 3 did not include QA samples such as PE samples and Matrix Spike/Matrix Spike Duplicate (MS/MSD) samples. The number of blind field duplicate (Field Dup) samples are included in the total number of samples in column 3. For example, of the 295 samples which were measured for metals, 9 of the 295 samples were blind field duplicate samples.
[2] - PE = Performance Evaluation Samples; MS/MSD = Matrix Spike/Matrix Spike Duplicate Sample; Dups = Blind Field Duplicate Samples.
[3] - Accuracy as measured in MS (matrix spike) and MSD (matrix spike duplicate) samples, which are measured at a frequency stated in the table.
[4]- Precision as measured in MS (matrix spike) and MSD (matrix spike duplicate) samples, which are measured at a frequency stated in the table.
[5] - Methods for the Determination of Metals in Environmental Samples, EPA/600/4-91/010, June 1991.
[6] - The number of field samples were revised by project members after January 6, 1997.

Target compounds and detection limits were determined in the QAPP **(1)** by using a screening carcinogenic effect for a 70 kg adult and a target cancer risk of $1 \times 10^{-6}$. Screening for non-cancer effects was performed for a 14.5 kg child using a target hazard quotient of 0.1. Fish consumption rates assumed for adults and children were 194 and 81 g/day, respectively, which correspond to the cumulative 97th percentile consumption rate. For chemicals that had both slope factors for estimating carcinogenic risk and reference doses for estimating non-carcinogenic impacts, separate tissue screening concentrations were calculated and the lower of the two values was used for the screening analysis. These tissue screening concentrations were then compared to the tissue contaminant data collected in the Columbia River Basin in the past ten years.

Chemicals that exceeded tissue screening concentrations included dioxins/furans, PCBs, organochlorine and organophosphorus pesticides, PAHs and other semivolatiles, trace metal and radionuclides. Based on this risk screening analysis, a decision was made to measure contaminant classes listed in Table 3 of the QAPP **(1)**. Table 2, and Tables 4 through 6 in the QAPP **(1)** provide a listing of individual target compounds in each of these classes.

After the draft study design document was completed, an analytical method (Method 1668) became available for measuring dioxin-like PCBs. This new EPA method was developed by the EPA Office of Water (OW) at the request of EPA Region 10 and under the direction of William A. Telliard of the OW Analytical Methods Staff. A list of target compounds and typical quantitation limits for most project samples are listed in Appendix A, Table A-3. It should be pointed out that World Health Organization (WHO) recently revised the list of dioxin-like PCB target compounds and toxicity equivalent factors (TEFs). PCB congener 81 has been added and PCB congeners 170 and 180 have been dropped from earlier lists of toxic PCB congeners.

The separate tissue screening concentrations calculated in the study design document were selected as the risk-based detection limit goals for this project with the following exception: In the design document, the fish consumption rates used to calculate the separate tissue screening concentrations were the 97th percentile from the CRITFC study. Because use of the 95th percentile was more in line with EPA guidance, the separate tissue screening concentrations in the design document were recalculated using the 95th percentile consumption rates. Table 2 and Tables 4 through 6 in the QAPP **(1)** contain the risk-based detection limit goals (formally the STCs)(shown in the tables as the "risk levels") calculated using the 95th percentile fish consumption rates. The actual quantitation limits that were achieved for most project samples are listed in Appendix A, Table A-3. It should be noted that “U” values reported in the project data base were determined using conventional data validation procedures as are described in Section 8.1 of the QAPP **(1)**. Specifically, the “U” values for metals and mercury are based upon the experimental determination of instrument detection limit as is defined in 40CFR Part 136, Appendix B. The “U” values for PCDDs/PCDFs and PCB congeners was determined experimentally in each sample by measuring the signal to noise ratio of the chromatography base line as is specified in Methods 1613B and 1668. The “U” values for all other organic target compounds was the lowest point of the 5 point initial calibration curve.

A list of radionuclides was not included in the original QAPP **(1)** due to lack of resources to pay for analytical measurements at the time. However, it was agreed at the scoping meeting that EPA would attempt to find resources for these analyses. Resources were found and an addendum to

the QAPP was prepared in September of 1997 **(2)**. Table A-3 in Appendix A provides a list of target radionuclides and detection limits which were measured in project samples.

As shown in Appendix A, Table A-3, several chemicals have detection limits that are above the risk level goals that were calculated. For this project, analytical methods were chosen to provide detection or quantitation limits which are as low as possible given available analytical methods and resources.

### 5.1.2 Station Locations by Global Positioning System

The position of each station was determined by using a global positioning system (GPS) in the autonomous (non-differentially corrected) mode. The positions of all stations, except for stations 10, 11, 13 and 14, were post-processed to obtain final positions accurate to within ± 3 meters. GPS station positions are listed in Appendix A, Table A-2.

## 5.2 Project Measurement Performance Criteria

The following objectives were measurement goals for the project:

### 5.2.1 Precision

Precision is the measurement of agreement among repetitive measurements of the same sample. For this project, precision was evaluated in two ways:

15. The relative percent difference (RPD) between matrix spike/matrix spike duplicate (MS/MSD) samples was calculated. As shown in Table 1, MS/MSD measurements were made at a frequency of one per twenty samples/composites. Since a total of 284 to 295 fish samples were measured, this results in a total of approximately 14 MS/MSD samples for each analytical group. Precision requirements for MS/MSD samples are listed in Table 3. It should be noted that every sample which was measured for PCDDs/PCDFs and PCB congeners were spiked with isotope-labeled matrix spike target compounds. Therefore, the nine blind field duplicate samples which were collected and measured can be used to determine the precision of isotope-labeled matrix spike target compounds as well as the native unspiked compounds which were measured in the field samples.

16. The relative percent difference (RPD) between field duplicate samples was calculated and the results are listed in Appendix B, Table B-2. The overall precision of PCDD/PCDF measurements in the 9 blind field duplicate samples was 21%. For PCB congeners the overall precision was 11%, for chlorinated pesticides and Aroclors the overall precision was 20%, for metals the overall precision was 22%, and for mercury the overall precision was 13%. For all measurements of the above functional chemical groups, the overall precision of all measurements was 18% for the 9 field duplicates. These results provide data users with a measure of expected variability of analytical data.

All 9 blind field duplicate samples which were measured for non-radionuclide target compounds were comprised of either FS or FW fish samples. There were not any WB samples among the 9 blind field duplicate samples which were measured for non-radionuclide target compounds. It should be noted that for the 2 blind field duplicate samples which were measured for radionuclide target compounds, these composite samples were prepared by splitting the composited WB ground fish tissue of one sample into two portions and using each portion as a unique sample.

For field duplicate samples and for matrix spiked and matrix spiked-duplicate samples, precision was measured as Relative Percent Difference (RPD). **(1)**

$$RPD = \frac{\text{Absolute } (R1 - R2)}{((R1 + R2)/2)} \times 100$$

R1 = Recovery for MS or duplicate 1, R2 = Recovery for MSD or duplicate 2

Precision requirements for the analysis of project MS/MSD samples are specified in Table 3 and varied between 30% and 50% depending upon the analytical group of target compounds. By contrast, the QAPP **(1)** required that precision for the analysis of blind field duplicate samples (see Appendix B, Table B-2) (consisting of the opposite fillets of the same fish) be less than 40 relative percent difference. Laboratory MS and MSD samples were prepared by each laboratory by taking a single sample and spiking it prior to sample extraction with a known amount of selected target compounds. This process was done twice, producing two spiked samples, a MS and a MSD. From the analysis of these three samples, ie, the unspiked, the MS, and the MSD, results of these measurements demonstrate accuracy and precision for these selected target compounds. The disadvantage in MS/MSD measurements was that they are known to the laboratory and MS/MSDs do not test precision of sampling, shipment, grinding, and compositing of samples. Whereas, blind field duplicates are blind to the laboratory and blind field duplicates test the entire system from field sampling to final sample analysis. The results of the assessment of precision results are discussed later in Section 8.2 of this QA Volume.

Table 4. Average Accuracy and Precision of MS/MSD Samples

| Chemical Group | Average Recovery | Average Percent Difference |
|---|---|---|
| AED-Pest Group | 62% | 24% |
| SV Group | 74% | 21% |
| GCP Group | 101% | 22% |
| Mercury | 99% | 6% |
| Metals | 105% | 4% |
| Chlorinated Pest-Aroclor Group | 86% | 13% |
| Average of Measurements, above. | 83% | 17% |

### 5.2.2 Accuracy

Accuracy is the degree of agreement of an experimental measurement with an accepted standard reference. Accuracy was evaluated by calculating the percent recovery (%R) of target analytes or isotope-labeled target compounds in spiked samples, and by the measurement of known target compounds in Performance Evaluation (PE) tissue samples.

$$\%\ \text{Recovery} = \frac{SQ - NQ}{S} \times 100$$

SQ = quantity found in spiked sample,
NQ = quantity found in native (unspiked) sample,
S = quantity of spike added to native sample

The accuracy requirements for MS/MSD samples for each measurement method are presented in Table 3 and in the QAPP **(1)**. The results of each MS/MSD measurement is listed in Appendix B, Table B-3. The average recovery of MS/MSD measurements is listed in Table 4. The overall average of all MS/MSD measurements was 83%. All accuracy requirements listed in the QAPP **(1)** were met. The results of the assessment of accuracy results are discussed later in Section 8.2 of this QA Volume.

As shown in Table 3, six Performance Evaluation (PE) samples (PE samples EDF-2524, EDF-2525, and EDF-2526) were required to be measured for chlorinated dioxins/furans and for the dioxin-like, PCBs by AXYS Laboratory. The measurement of these PE samples was conducted at the beginning and end of the project. The results of the measurement of these PE samples are listed in Table 5.

### 5.2.3 Representativeness

Representativeness is the degree to which data from the project accurately represent a particular characteristic of the environmental matrix which is being tested. For example, representativeness is the degree to which data accurately and precisely represent a characteristic of a population, a matrix, a natural variation at a sampling location, or an environmental condition. Acceptable representativeness is achieved through adequate sampling program design and QAPP design. Goals for representativeness are primarily met by ensuring that, given available resources, sampling locations are properly selected and that a sufficient number of tissue types and fish species are collected.

The design of the QAPP required the collection of triplicate composite samples at most sampling sites. The purpose of measurement of three samples at each site was to measure the variation of different types of samples at each sampling site and to calculate the true mean of measurement results. Table C-1 in Appendix C lists the average measured value and standard deviation of target compounds in the first 10 composite groups. Appendix C, Table C-1 presents the variability of the first 10 composite groups. As is discussed and is presented graphically in other volumes of the Project Final Report, the measurement of replicate samples was one on the methods from which the representativeness of project samples was assessed.

### 5.2.4 Completeness

Completeness is the percentage of valid results obtained as compared to the total number of samples taken for a parameter. Completeness requirements for this project are presented in Table 1.

$$\% \text{ Completeness} = \frac{\text{\# of valid results}}{\text{\# of samples taken}}$$

### 5.2.5 Comparability

Comparability is a qualitative characteristic expressing the confidence with which one data set can be compared with other data sets. In this regard, measurements of PCDDs/PCDFs and dioxin-like, PCBs from this project may not be comparable with PCDD/PCDF and dioxin-like, PCB data measurements from previous projects because new and improved state-of-the-art methods such as Methods 1613B and 1668 were used in this project to measure samples. In addition, data from previous projects have not always been validated and qualified to determine data quality and data useability. Therefore, a comparability goal for the measurement of PCDDs/PCDFs and non-coplanar PCBs for this project cannot be set. By contrast, project data for the measurement of metals, pesticides/PCBs and semi-volatile organics should be more comparable to previous data from the analysis of Columbia River basin fish. A comparability goal of 70% was set for these non-PCDD/PCDF and non-coplanar PCB data.

### 5.2.6 Other Measurement Performance Criteria

In addition to the specific measurement objectives discussed above, Section 9.4 of the QAPP specifies that all quality control requirements of each method which are referenced in Table 1 shall be obtained and reported by each analytical laboratory. These laboratory QC measurements include the use of surrogate compounds, internal standards, recovery standards, matrix spike compounds, isotope dilution labeled internal standards, instrument calibrations, and method blanks.

An additional data quality objective of the project was to obtain validated PCDD/PCDF data which were free of expected chlorinated chemical interferences such as polychlorinated diphenyl ether (PCDE) interferences to the measurement of PCDD/PCDF target compounds. Therefore, one of the additional primary data quality objectives in this QAPP was for AXYS Laboratory to remove chemical interferences to the measurement of 2,3,7,8-TCDF, which is the PCDD/PCDF isomer which has been found in fish tissue in the Columbia River system. Previous 2,3,7,8-TCDF data from the Columbia River system have often been contaminated with PCDE chemical interferences.

Insert Table 5 here

Table 5. Results For The Measurement of PE Samples EDF2524, EDF-2525, and EDF 2526

# Chapter 6.0 HOMOGENIZATION OF INDIVIDUAL FISH AND COMPOSITES AND DISTRIBUTION OF HOMOGENIZED SAMPLES

Upon receipt of fish and egg samples from the Field Operations Manager, AXYS Laboratory homogenized tissue samples, prepared sample aliquots, and distributed these sample aliquots to the appropriate analytical laboratories for analyses.

## 6.1 General Considerations for Handling Samples

Fish samples and homogenized samples were handled following the guidance provided in sections 7.2.1 (General Considerations) and 7.2.1.3 (Samples for Both Organics and Metals Analyses) of Reference **(7)** (see Attachment 7 of the QAPP **(1)** for a copy of these sections of Reference **(7)**). AXYS was required to disassemble the tissue grinder (auger, auger housing, orifice plate, and any implement used to push tissue through the grinder) and clean these parts using an AXYS standard operating procedure (SOP) after each sample (individual fish or fish/egg composite) had been homogenized.

## 6.2 General Considerations for Preparing Composites

All of the right side fillets or whole fish or eggs that were a part of a given composite were homogenized together. This provided information on the weighted mean of the chemical residue in the batch of fish which were sampled. Information on contaminant levels provided by the above, batch method (which includes information from the entire fillet or wholebody of each fish in a composite), provided a more appropriate estimate of exposure for the Native Americans. The above, compositing method was also easier to implement in the laboratory because it saved sample preparation time and resources and maximized the amount of tissue available after grinding smaller fish.

## 6.3 Sample Homogenization

Whole fish, fish fillets, and eggs were ground and homogenized using tissue grinders which were similar to a Hobart Model 84186 commercial meat grinder. During the three year period that project fish tissue samples were ground and composited at the AXYS Laboratory, it was necessary to replace the original tissue grinder, a ½ horsepower (HP) OMAS Triticarne grinder, with larger 2.0 HP and 3.0 HP tissue grinders. During the three year period, the following tissue grinders were used to prepare project fish composites:

- 0.5 HP OMAS Grinder, model: Triticarne
- 2.0 HP Berkel Grinder
- 3.0 HP Berkel Grinder, model TCA-32, serial number S2457

The face plate and cutting blades of all three grinders were made of stainless steel. The auger of the ½ HP and 3.0 HP grinders were also made of stainless steel. The auger of the 2.0 HP grinder was made of cast iron plated with chrome.

Possible contamination of project tissue samples with ether PCB congeners or especially metals was a concern. Therefore each grinder was tested for contamination of samples by conducting an equipment rinsate test. This test consisted of passing a liter of reagent water through each grinder and collecting the rinsate water in a stainless steel bowl and allowing the rinsate water to stand in the bowl for ten minutes. For PCB congener measurements, the entire one liter of rinsate water was extracted according to Method 1668 and analyzed by high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS). For metals measurements, the rinsate water was acidified with nitric acid to a pH of less than 2 and placed in high density polyethylene bottles and shipped to the EPA laboratory at Manchester for analysis using EPA Method 200.8. Table 6 shows the results of the analysis of grinder equipment rinsate blanks for the three grinders and stainless steel bowl, as well as the reagent water that was used for the contamination test:

Generally, Table 6 shows that all measured levels in these grinder rinsate blanks were low. Manganese and nickel were higher in 3 HP Grinder rinsate water. Copper and lead were higher in 2 HP grinder rinsate water. Aluminum and zinc were higher in ½ HP grinder rinsate water. PCB 105 was slightly higher in the ½ HP and 3 HP grinder rinsate water. According to the QAPP (1), the calculated risk level of aluminum, copper, and zinc are at concentrations above 600 mg/kg. Therefore, the measurement of these three metals in project tissue samples should not be affected by small amounts of contamination from these tissue grinders. However, in the case of lead, the calculated risk level was 7.7 mg/kg (7.7 PPM). Lead was measured in rinsate water from the 2 HP Grinder at 77 ug/l (77 PPB). Lead values varied in project tissue samples between 0.01 mg/kg and 1.15 mg/kg which is below the calculated risk level of 7.7 mg/kg. Some lead measurements in project tissue samples may have been contaminated by the 2 HP Grinder. Data users should use caution in using lead measurement results. It is possible to determine from AXYS analytical reports which grinder was used to homogenize each project sample. Therefore, data users can determine which grinder was used to homogenize specific project samples.

For larger fish samples, the fish tissue was first cut into small pieces and then these fish tissue pieces were ground in the equipment specified. After the first grinding, the process tissue was divided into quarters, opposite quarters mixed together by hand, and the two halves mixed together. At a minimum, each composite sample was processed through the grinder three times and hand mixed with a stainless steel spoon three times. If chunks of tissue were observed, the grinding and homogenization was repeated until the composite sample appeared to be homogenous. No chunks of tissue or pieces of skin remained in composited samples.

Egg samples were ground a minimum of three times.

AXYS Laboratory prepared an adequate amount of homogenate to meet the requirements for analysis as specified in Table 3 (column titles "Containers").

## Table 6. Equipment Rinsate Blanks For Three Project Grinders [1]

| Element | Reagent Water | Bowl Rinsate Blank | ½ HP Grinder | 2 HP Grinder | 3 HP Grinder |
|---|---|---|---|---|---|
| Al | 2.0 U | 2.0 U | **8.7** | 2.0 U | 2.0 U |
| As | 0.1 U | 0.1 U | 0.1 U | **0.1** | 0.1 U |
| Cd | **0.058** | 0.04 U | **0.074** | **0.063** | **0.062** |
| Cr | 1.0 U | 1.0 U | 1.0 U | 1.0 U | **1.2** |
| Co | 0.01 U | 0.01 U | **0.026** | **1.83** | **1.3** |
| Cu | 0.5 U | 0.5 U | **4** | **25.2** | **1.9** |
| Pb | 0.1 U | 0.1 U | **5.3** | **77** | 0.1 U |
| Mn | 0.1 U | 0.1 U | **0.38** | **3.1** | **5.9** |
| Ni | 0.3 U | 0.3 U | **19.6** | **6.7** | **57** |
| Zn | 1.0 U | 1.0 U | **4.2** | **2.2** | **1.8** |
| PCB 77 | 0.03 U | 0.03 U | 0.04 U | 0.03 U | 0.03 U |
| PCB 123 | 0.01 U | 0.03 U | 0.05 U | 0.01 U | 0.04 U |
| PCB 118 | **1.07** | **0.87** | 0.04 U | **0.86** | **0.9** |
| PCB 114 | 0.01 U | 0.05 U | 0.06 U | 0.02 U | 0.05 U |
| PCB 105 | 0.01 U | 0.04 U | **0.46** | 0.01 U | **0.37** |
| PCB 126 | **0.07** | 0.04 U | **0.05** | 0.01 U | 0.03 U |
| PCB 167 | 0.01 U | 0.075 | 0.01 U | 0.01 U | 0.01 U |
| PCB 156 + 157 | **0.4** | 0.05 U | 0.02 U | 0.02 U | 0.02 U |
| PCB 169 | 0.01 U | 0.03 U | 0.01 U | 0.01 U | 0.01 U |
| PCB 180 | 0.03 U | **0.39** | 0.02 U | 0.03 U | **0.6** |
| PCB 170 | 0.03 U | 0.03 U | 0.03 U | **0.16** | 0.02 U |
| PCB 189 | 0.01 U | 0.02 U | 0.02 U | 0.03 U | 0.02 U |

[1] - For metals measurements, units are in ug/l. For PCB Congener measurements, units are in pg/l.

## 6.4 Sample Distribution

AXYS Laboratory prepared sample aliquots (as described in section 8.5 of QAPP **(1)**) immediately after homogenization was completed and then distribute these sample aliquots to the EPA Region 10 Laboratory for chemical analyses. Unless aliquots were measured immediately, they were frozen and stored in a secure location at ≤-20° C until transfer to the EPA laboratory for analysis or until analyses was begun by AXYS Laboratory. Approximately 400 grams of each homogenate (i.e., that not put into sample aliquot jars) was placed into each of two (2) wide mouth glass 16 ounce jars and stored at ≤-20° C by AXYS Laboratory for 6 months. This portion of sample homogenate which were designated for radionuclide measurements was shipped to the EPA Region 10 Laboratory and subsequently sent to the radionuclide laboratories for chemical analyses. The shipping directions in Section 4.8 were followed. Glass jars were securely packed to avoid breakage during shipment.

## 6.5 Sample Containers and Labels

AXYS Laboratory placed approximately fifty (50) grams of homogenized sample into each of 26 clean wide mouth 2 ounce glass sample jars. The laboratory left sufficient headspace in each jar such that expansion during freezing did not cause jars to break. A total of 4 jars (2 for PCDDs/PCDFs analyses and 2 for dioxin-like PCB analyses) were retained by AXYS Laboratory for analyses of PCDDs/PCDFs and dioxin-like, PCBs. The laboratory sent the 22 remaining jars to Region 10 EPA's laboratory.

EPA used up to twelve of these jars for the analyses of pesticides/PCBs, semivolatiles, PAHs, Target Analyte List (TAL) inorganics, and mercury.

AXYS Laboratory affixed bottle labels firmly to each sample container and lid. Each container label and lid tape were filled out with the appropriate sampling information. The following list identifies the information that was written on each container and lid label:

**Figure 6. EPA Lid Label**

* EPA Composite Sample Number: (8 digit code)

* Sample Processing Date: MM/DD/YY

**Figure 7. EPA Bottle Label**

* EPA Composite Sample Number: (8 digit code)

* Station Location:

* Sample Processing Date: MM/DD/YY

* Laboratory Samplers Initials:

* Type of Sample:

  1. Whole body,
  2. Fillet with skin
  3. Fillet without skin,
  4. Eggs

Each sample container was labeled before filling the bottles with tissue. To ensure that the bottle labels were attached firmly, the laboratory wrapped an extra layer of clear strapping tape around the bottle completely sticking the tape to itself.

## 6.6 Documentation for Sample Homogenization, Aliquot Preparation, and Distribution of Aliquots

### 6.6.1 Homogenization

The relevant portions of the Sample Processing Record discussed in Section 6.2 and in Attachment 9 of the QAPP **(1)** were completed by personnel at AXYS Laboratory responsible for homogenization. Each record was signed and dated upon completion. Copies of this Record were forwarded to the EPA Work Assignment Manager within 7 calendar days after each batch of samples was prepared for analyses. In addition, the laboratory prepared a narrated video tape showing the procedures and equipment used during each stage of the initial sample processing, including all steps in grinding, mixing and homogenizing, and in cleaning of all equipment. A copy of this video was sent to the EPA Project Manager after the first batch of samples has been prepared for analysis. Each sample composite was photographed and sent to the Field Operations Manager for inspection.

### 6.6.2 Preparation of Sample Aliquots

AXYS Laboratory maintained accurate records for the preparation of samples aliquots after tissue grinding was completed. The Sample Aliquot Record listed in Attachment 12 of the QAPP **(1)** was completed by AXYS Laboratory. The Composite Sample ID used on the Sample Aliquot Form was designated by EPA on the Sample Processing Record. The Sample Aliquot Record was used to record the total composite homogenate weight for each composite sample and the total number of bottles filled. This record was signed and dated. Completed copies of the

Sample Processing Record and the Sample Aliquot Record for each sample are listed in the AXYS PCDD/PCDF analytical report for each sample processed.

### 6.6.3 Sample Aliquot Transfer

Laboratory personnel at each of the analytical laboratories were responsible for the care and custody of sample aliquots from the time they were received until the samples were depleted or disposed of. Chain-of-custody procedures were used at each laboratory. For sample aliquots sent to the EPA Laboratory for analysis or archiving, the original field COC Form(s) were signed, enclosed in plastic, taped to the inside lid of the cooler in which the samples were sent, and COC seals were applied to the shipping container. All samples/sample aliquots were shipped on dry ice using the procedures written in Section 7.0 of the QAPP **(1)**. Upon receipt at the EPA laboratory, the sample receipt and chain-of-custody procedures listed in Attachment 11 of the QAPP **(1)** were followed.

# Chapter 7.0 LABORATORY MEASUREMENTS

A summary of the project chemistry measurements are presented in Appendix B-5. As previously discussed, the analysis of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzo-p-furans isomers (PCDDs/PCDFs), percent lipids, and dioxin-like, PCB congeners were conducted by AXYS Laboratory which was subcontracted by the primary EPA contractor, Tetra Tech. Tetra Tech was replaced during the mid-phase of the project with the contractor, EVS Environmental Consultants. Pat Cirone was the Work Assignment Manager (WAM) for each of these primary EPA contracts. The remaining analyses were performed by the EPA Region 10 laboratory at Manchester, WA, the EPA National Air and Radiation Environmental Laboratory (NAERL) in Montgomery, Alabama, and Barringer Laboratory in Golden, Colorado.

Laboratory analytical protocols specified for this project are referenced in Table 3 and in the specifications below. Each analytical laboratory which measured project samples grouped analytical reports into Sample Delivery Groups (SDGs). SDGs are usually groups of 20 or less samples.

The following procedure was used by each analytical laboratory prior to removing a ground sample from a sample bottle for analysis of target compounds:

- Place sample container containing ground fish tissue/eggs in a 34$^{o}$F to 40$^{o}$F refrigerator 24 hours prior to removing aliquot of sample.
- Remove sample bottle from the refrigerator and place on the laboratory bench at room temperature until all ice crystals in the sample bottle have melted.
- Hand stir the thawed tissue vigorously with a clean 1/4 inch solid glass rod for 1 minute.
- Immediately remove sample containing tissue and liquid from sample bottle for weighing and laboratory analysis.
- Fill out a Corrective Action Form (see Attachment 18 of QAPP **(1)**) if any sample bottles contain either chunks of fish tissue or pieces of fish skin.

All inspections of ground, composited samples by EPA at the EPA Regional Laboratory demonstrated the all project samples were correctly prepared by AXYS Laboratory according to specifications of the QAPP **(1)**.

## 7.1 Target Analytes

The PCDDs/PCDFs and PCB dioxin-like, congeners measured by AXYS laboratory are listed in Appendix A, Table A-3. The EPA Region 10 Laboratory measured the chemical groups of

organics and inorganics listed in Table 3. Specific target compounds for each group of chemical compounds are listed in Appendix A, Table A-3. For this project which requires the measurement of pesticide and semi-volatile (SV) organics in fish tissue, it was difficult to specify the list of target compounds, because some project samples such as Pacific Lamprey contained 21% by wet weight of lipid compounds. These naturally occurring lipids and fatty acids can interfere with the measurement of many organic target compounds. Extract clean-up procedures such as the use of gel permeation chromatography, Jordi-gel, Florisil and silica gel were used to remove analytical interferences such as lipids and fatty acids. Project quality control measurements for the recovery of laboratory matrix spiked target compounds provided critical information on the loss of target compounds due to the required use of lipid removing clean-up procedures.

## 7.2 Analytical Methodology

### 7.2.1 PCDDs/PCDFs

Method 1613B was developed by the United States Environmental Protection Agency's Office of Science and Technology for isomer-specific determination of the 2,3,7,8-substituted, tetra- through octa-chlorinated, dibenzo-*p*-dioxins and dibenzofurans in aqueous, solid, and tissue matrices by isotope dilution, high resolution capillary column gas chromatography (HRGC)/high resolution mass spectrometry (HRMS).

As part of the measurement of PCDDs/PCDFs by AXYS Laboratory, all samples which were measured for PCDDs/PCDFs were also measured for percent lipids according to the procedure described in EPA Method 1613B. Briefly, this procedure requires that 20 grams of fish sample be mixed with 30 to 40 grams of anhydrous sodium sulfate, the mixture stirred until thoroughly mixed, and then the mixture extracted with a 1:1 mixture of methylene chloride and hexane using a Soxhlet extractor for 18 to 24 hours. After extraction, the solvent was evaporated using a water bath at 60$^{o}$C until a constant sample weight was obtained. It should be noted that this lipid determination procedure is the same procedure which was used by EPA in the National Dioxin Study of 1990 (see EPA publication EPA/600/3-90/022). Other percent lipid procedures such as the three extraction methods described in EPA Method 8290 would have produced different percent lipid results because of the different extraction solvents used and different extraction conditions. Users of lipids data from other projects should be aware that percent lipids data from all projects will not be comparable due to the use of non-compatible analytical procedures for some data sets.

The seventeen 2,3,7,8-substituted CDDs/CDFs listed in Appendix A, Table A-3 may be determined by this method. The detection limits and quantitation levels in the method are usually dependent on the level of interferences in the sample matrix rather than instrumental limitations. For this project, the experimental detection limit for most samples was between 0.01 to 0.05 ng/kg of wet fish tissue.

Tetra Tech/EVS was responsible for subcontracting to AXYS Laboratory which was responsible for analysis of PCDDs/PCDFs isomers and dioxin-like, PCBs according to specifications in the following document (see also Attachment 13 of the QAPP (1))]:

> USEPA 1996b. EPA Region 10 Statement of Work For the Measurement of 17 Polychlorinated Dibenzo-p-dioxins and Polychlorinated Dibenzo-p-furans (PCDDs/PCDFs) In Fish Tissue By High Resolution GC/High Resolution Mass Spectrometry Using Method 1613B (Revision 2.1, 6/6/96). **(9)**

Attachment 13 of the QAPP provided specifications for the subcontract laboratory and permitted EPA to validated PCDD/PCDF data according to the following data validation guidelines:

> USEPA 1995. EPA Region 10 SOP For the Validation of Polychlorinated Dibenzofuran (PCDD) and Polychlorinated Dibenzofuran (PCDF) Data, Revision 1.4, December 7. **(10)**

Tetra Tech / EVS was responsible for determining if the subcontract laboratory, AXYS Laboratory, had a QA Program which would support the QA and technical requirements of the QAPP.

The quantitation limits specified in the QAPP **(1)** for the measurement of 2,3,7,8-TCDD and 2,3,7,8-TCDF required that AXYS Laboratory achieve a Minimum (Quantitation) Limit (ML) of 0.2 ng/Kg (wet weight) for isomers 2,3,7,8-TCDD and 2,3,7,8-TCDF. This lower ML was achieved by the use of a low initial calibration point of 0.1 ng/ml and an ultra-low sensitivity HRMS system. The laboratory used the same calibration standards with the same lot number, for all internal standards and labeled standards used in measuring the initial calibration curve, verification standards, field samples, and method blanks on both the primary GC column and on the secondary confirmation GC column. As requested in the QAPP, a low level calibration solution was included in the linearity series in order to quantify target analytes at concentrations which were 0.20 times below the CS1 concentrations of Method 1613B. The percent RSD of the resulting 6-point calibration curve was less than 20% as is required by Method 1613B.

Project samples were extracted according to Method 1613B. Clean-up of sample extracts included gel permeation chromatography, an acid/base wash, two alumina column clean-ups, and an activated carbon/celite back extraction. The final volume of the sample extracts was 20 µl; 1 µl was injected onto the GC column. None of the samples required dilution.

Volumes of extracts before and after each clean-up step were maintained at constant levels to standardize sample treatment. Extract volumes before and after the various clean-up treatments are summarized below.

Table 7. Clean-Up Steps of PCDD/PCDF Extracts

| CLEAN-UP PROCEDURE | INITIAL VOLUME | FINAL VOLUME | ROTARY EVAPORATION |
|---|---|---|---|
| Acid/Base Wash | 5 ml, toluene | 50 ml, hexane/toluene | just to dryness, redissolved in 1.5 ml hexane |
| 1st Alumina Column | 1.5 ml, hexane | 55 ml, 1:1 DCM:hexane | to 1 ml |
| Carbon/Celite | 1 ml, hexane | 50 ml, toluene | just to dryness, redissolved in 1.5 ml hexane |
| 2nd Alumina Column | 1.5 ml, hexane | 55 ml, 1:1 DCM:hexane | to 500 µl, then by Nitrogen blowdown just to dryness |

According to AXYS, analysis of the labeled surrogate standard and recovery standard solutions showed a discrepancy in the amount of $^{13}C_{12}$-1,2,3,4-TCDD recovery standard added to the extracts before instrumental analysis as compared to the nominal values quoted for the calibration series' standards. This affected the surrogate standard percent recovery determinations for the tetra- and penta- substituted carbon-13 labeled dioxins and furans -- they were found to be low by a factor of 1.23. This discrepancy did not affect the quantification of the target native analytes in the samples. In order to correct this discrepancy for the sample analysis reports, values for "concentration found" and "percent recovery" of tetra- and penta-substituted carbon-13 labeled dioxins and furans standards and clean-up standards were multiplied by 1.23 in the data reported by AXYS.

The sum of the area counts of the two masses for each of the two instrument recovery internal standards for samples, blanks, and standards did not vary by more than a factor of four (-25% to +400%) from the sum of the associated average areas from the six initial calibration standards.

Measurement results for 2,3,7,8-TCDF in project chemistry measurements database are from measurements on the secondary GC column, DB225.

EPA Method 1613B specifies certain requirements and guidelines for the positive identification of PCDD and PCDF isomers. The most frequently encountered interfering compounds to the measurement of PCDDs and PCDFs are chlorinated substances such as polychlorinated diphenyl ethers (PCDEs), polychlorinated biphenyls (PCBs), polychlorinated alkyldibenzofurans, and polychlorinated napthalenes that may be found at concentrations several orders of magnitude higher than the analytes of interest. Interferences are such a major problem to Method 1613B, that the method requires that PCDE interference ions be scanned at the same time that PCDD and PCDF mass ions are measured. No PCDE interferences were noted in project samples after clean-up of extracts. However, AXYS reported interferences from polybrominated diphenyl ether isomers (PBDEs) in several sample extracts. PBDEs were reported by the Manchester

Laboratory in extracts measured by Method 8085 GC/AED (see Section 7.2.4, below, for additional details). The presence of PBDEs did not cause lock mass interferences or quantitation problems for the measurement of PCDDs/PCDFs.

AXYS Laboratory provided data packages which addressed all the data assessment requirements of Method 1613B and the EPA data validation SOP **(10)**.

### 7.2.2 Dioxin-Like, PCBs

Draft EPA Method 1668 was developed for the project by William A. Telliard at the EPA Office of Water, EPA Headquarters. Overall, the draft method produced useable PCB congener data which met the requirements of the QAPP **(1)**. This method is for determination of the toxic polychlorinated biphenyls (PCBs) in water, soil, sediment, sludge, tissue, and other sample matrices by high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS). The method is for use in EPA's data gathering and monitoring programs associated with the Clean Water Act, the Resource Conservation and Recovery Act, the Comprehensive Environmental Response, Compensation and Liability Act, and the Safe Drinking Water Act. The method is based on a compilation of methods from the technical literature and on EPA Method 1613B.

Method 1668 was designed to measure the 13 dioxin-like PCB congeners listed in Appendix A, Table A-3. Detection limits and quantitation levels in this method are usually dependent on the level of interferences rather than instrumental limitations. For this project, the experimental detection limit for many of the PCB congener target compounds was between 0.02 to 1.0 ng/kg of wet fish tissue.

Tetra Tech (Contractor) was responsible for subcontracting to AXYS Laboratory which was responsible for Method 1668 measurements. These analyses were conducted according to the specifications stated in the QAPP **(1)** and the following document:

> USEPA 1997b. Method 1668, Toxic Polychlorinated Biphenyls (PCBs) By Isotope Dilution HRGC/HRMS, Draft Revision, March. **(11)**

Overall, Method 1668 produced useable PCB congener data which met the requirements of the QAPP **(1)**, however, like any draft analytical method, AXYS encountered a number of problems associated with QC limits in both the method, and purity of calibration standards from commercial sources. For example, some acceptance criteria listed in DRAFT Method 1668 were not correct. The calibration verification acceptance criteria given in Table 6 of Method 1668 were incorrect. These criteria appeared to have been based on concentrations in the precision, accuracy, and recovery standard rather than on the concentrations in the calibration solutions. AXYS derived suitable acceptance criteria by encompassing plus/minus twenty-five (25) percent deviation from actual concentrations. Therefore, the system was judged to be in control if all calculated concentrations for the calibration verification run fell within 75 to 125 percent of the actual CS3 solution values, which are listed in Table 4 of Method 1668.

The "Test" concentrations of the clean-up standards, 13C-PCB 81 and 13C-PCB 111, given in Table 6 of Method 1668 were incorrect. The actual concentrations are 50 ng/ml and 250 ng/ml,

respectively, not 20 ng/ml and 100 ng/ml as shown. The clean-up standard acceptance specifications for initial precision and recovery tests, ongoing precision and recovery tests, and samples in Tables 6 and 7 of Method 1668 were also incorrect. AXYS derived acceptance criteria by multiplying the specifications given in these tables by the ratio of the actual "Test" concentrations. For example, the acceptance criterion used for the standard deviation of 13C-PCB 81 in Initial precision and recovery tests was: 7.2 x (50/20) = 18 ng/ml.

The "Test" concentration for 13C-PCB 189 given in Table 6 of Method 1668 was incorrect. It should have been 100 ng/ml rather than 200 ng/ml. The precision accuracy and recovery standard used by AXYS contained 100 ng/ml. There were not any acceptance criteria listed for 13C-PCB 209 in Table 6, although the method specifies that 13C-PCB 209 be carried through the analytical analysis.

Instructions given in section 7.10.3 of Method 1668 for preparation of the diluted surrogate spiking solution were incorrect; the dilution factor required to produce the surrogate concentrations listed in Table 3 of Method 1668 is 500, not 50 as was stated in the draft method. AXYS spiked surrogates into project samples at the levels specified in Table 3 of Method 1668.

All required standards and isotopes used to measure samples using Method 1668 were commercially available, however, preliminary standards validation work carried out by AXYS indicated inaccuracies in the chemical standards provided by Cambridge Isotope Laboratories (see Table 8). Cambridge Isotope standards were tested for internal consistency by measuring a mixture of target, surrogate, clean-up, and internal standards against the calibration standard. This test resulted in significant overestimation of PCB 114 and underestimation of PCB 170 which could attribute to inconsistencies between the standards. Standards were also tested for absolute accuracy by analysis of the CLB-1 series of certified reference standards produced by the National Research Council of Canada (NRCC). This test resulted in underestimation of PCBs 77, 118 and 180 and overestimation of PCB 114. One further absolute accuracy test was conducted using a non-ortho substituted PCB standard validated by AXYS against standards obtained from Environment Canada and the World Health Organization (WHO); this test resulted in slight underestimation of PCBs 77 and 169. The results of these tests are summarized in Table 8. These results were provided by AXYS to Cambridge Isotopes, who advised AXYS that final validation of the standards had not been completed. AXYS has recommended that further QC testing using additional reference standards be carried out to validate the concentrations in the Method 1668 standards provided by Cambridge. Sample results have not been corrected for the above trends noted by AXYS. However, one of the recommendations of this Report is that EPA secure sources of native and labeled PCB congener standards which are certified for purity and accuracy.

Table 8. Evaluation of Purity of PCB Congener Standards

| Congener | Consistency Check [1] | Accuracy Check [2] | Accuracy Check [3] |
|---|---|---|---|
| PCB 77 | 116 | 73 | 92 |
| PCB 123 | 99 | | |
| PCB 118 | 97 | 66 | |
| PCB 114 | 136 | 170 | |
| PCB 105 | 102 | 103 | |
| PCB 126 | 100 | | 95 |
| PCB 167 | 101 | | |
| PCB 156/157 | 102 | 95 | |
| PCB 169 | 101 | | 85 |
| PCB 180 | 101 | 86 | |
| PCB 170 | 88 | 97 | |
| PCB 189 | 97 | 98 | |

1. Analysis of Cambridge solutions as a set - results indicate the degree to which the Cambridge solutions are "matched".
2. Analysis of NRC CLB-1 certified standard
3. Analysis of AXYS Reference Solution

Analysis by high resolution MS was carried out using a VG 70 and a VG Ultima high resolution mass spectrometer each equipped with a HP 5890 gas chromatograph, a CTC autosampler and a VAX 3100 data system.

Chromatographic separations were performed using an SPB-Octyl capillary column (30m, 0.25 mm i.d., 0.25 μm film thickness) as the primary column. In those cases where a response was noted for the target pair PCB 156/157, further analysis to determine these compounds was performed using a DB-1 (30m, 0.25 mm i.d., 0.25 μm film thickness) column. The mass spectrometer was operated in the EI mode using Selected Ion Monitoring (SIM) to enhance sensitivity, acquiring the ions listed in Table 8 of Method 1668 Draft Revision 10/4/95, for each target analyte and surrogate standard. A split/splitless injection sequence was used. The final volume of the sample extracts was 20 μl; 1 μl was injected onto the GC columns.

The high resolution mass spectrometer at AXYS was operated in a mass-drift correction mode using perfluorokerosene to provide lock-masses which prevented the high resolution mass spectrometer from drifting off mass calibration. Some samples showed lock-mass interferences during instrumental analysis, however these lock-mass interferences did not occur in a region which was used to measure target compound peaks. Therefore, the mass resolution stability of the instrument was maintained during all sample measurements.

Several project samples indicated an acid/base silica column was required to minimize lock mass interferences. Consequently, this clean-up option was incorporated into the routine clean-up procedure. The column clean-up sequence was:

- gel permeation column
- Florisil column
- alumina column
- acid/base layered silica gel.

Despite exhausting all clean-up options, minor lockmass interferences were seen in some of the chromatograms, however, they did not interfere in areas of the chromatograms which were used for quantification of target compounds. Details of each clean-up procedure have been provided by AXYS -- Method CL-T-1668/Ver 2 Oct/96.

An initial calibration curve consisted of five concentration points for each analyte. The averaged response factor for analytes was measured by isotope dilution. General estimated detection limits of 0.05, 0.25, 0.5 and 0.5 pg/g were used for tetra, penta, hexa and hepta chlorinated PCBs, respectively. Where sample specific detection limits calculated from actual analysis data exceeded these values, sample specific detection limits were reported instead. Sample specific detection limits were determined from the analytical data as follows: the first minute in the primary and secondary m/z channels that was free of any detectable peaks was used to calculate a standard deviation of the instrumental noise. This standard deviation was then multiplied by a factor of three (3) to estimate the minimum detectable signal, by height, for a compound. The minimum height was then converted to a concentration using the same calculation used to convert analyte peak areas to concentrations (but using peak heights instead of areas). The estimated detection limits (EDLs) for PCB 126 and PCB 169 were generally higher than for other congeners due to matrix interferences.

The PCB 156 and 157 concentrations from the SPB-Octyl column are actually the sums of these two co-eluting isomers. The concentrations of individual PCB 156 and 157 congeners were determined on the DB-1 column which was the secondary GC column.

Recovery of 13C-PCB 180 was sometimes outside the acceptance range in selected project samples due to the presence of a co-eluting compound. In many cases surrogate recovery trends indicated the presence of interfering compounds even when recoveries fell within specifications. An interfering compound was observed to affect native target compound PCB 180 as well as the surrogate. For this reason, the normal Method 1668 protocol of dilution and quantification against an internal standard was judged inappropriate. When interferences were present on the primary column, PCB 170 and 180 were reported from measurements on the secondary column, which separated the interfering compound from the target analytes.

The response for PCBs 118, 105, 170, and 180 exceeded the calibration range in some cases. AXYS diluted and re-analyzed these extracts using the internal standard method.

Isomer specificity requirements stated in Method 1668, Section 10.4 were met.

Similar to the measurement of PCDDs and PCDFs, the dioxin-like, PCB congeners were validated by EPA Region 10 according to the following validation guidelines which were developed by Region 10 :

> USEPA 1995. EPA Region 10 SOP For the Validation of Method 1668 Toxic PCB Congeners, Revision 1.0, December 8. **(12)**

### 7.2.3 Non-Acid Labile Chlorinated Pesticides/Aroclors Using GC/ECD and Method 8081

The Region 10 Laboratory measured the chlorinated pesticides and PCB mixtures (as Aroclors) listed in Appendix A, Table A-3 using fused-silica, open-tubular, capillary columns with electron capture detectors (ECD). When compared to the use of packed GC columns, these GC columns offered improved resolution, better selectivity, increased sensitivity, and faster analysis. After clean-up, extracts were analyzed by injecting a 1-µl sample into the gas chromatograph with an electron capture detector (GC/ECD).

Homogenized tissue samples were extracted utilizing the Soxhlet technique as described in the "National Study of Chemical Residues in Fish", EPA 823-R-92-008a, September 1992. This extraction procedure was analogous to SW -846 Method 3540B. Extract volumes were split with one half of the volume used for non-acid labile Method 8081 chlorinated pesticides and aroclors and one half of the volume for acid labile Method 8085 AED pesticides. These AED extracts were sealed in containers and kept in a laboratory freezer. Dieldrin, endrin, endrin aldehyde, endrin ketone, endosulfan, endosulfan I, endosulfan II, and endosulfan sulfate which are acid-labile target compounds, were measured in the acid-labile AED fraction. By separating the pesticides into a non-acid-labile fraction and an acid-labile fraction, lower quantitation limits could be achieved for the Method 8081 non-acid-labile fraction and more pesticide target compounds could be measured in the Method 8085 acid-labile fraction using AED analysis. The disadvantage in measuring two pesticide fractions was that the quantitation limit for dieldrin, endrin, endrin aldehyde, endrin ketone, endosulfan, endosulfan I, endosulfan II, and endosulfan sulfate was increased by a factor of ten to 33 ug/kg. These expected quantitation limits were stated in Table 11 of the QAPP**(1)**. Another disadvantage of this analytical scheme was that acid-labile pesticides such as dieldrin, endrin, endosulfan, and diazinon were only measured in 135 project samples, whereas, non-acid-labile chlorinated pesticides such as 4,4'-DDE were measured in every project sample**(1)**.

Extracts for chlorinated pesticides/Aroclors listed in Appendix A, Table A-3 required Florisil® clean-up (SW-846 Method 3620A) of half of the extract (the other half of the extract was archived in a refrigerator), generating two elution fractions using hexane/ethyl ether as the eluant system. During the initial half of the CRITFC Project, the first fraction, 0% Diethyl ether fraction (100% hexane), was treated with concentrated sulfuric acid (SW-846 Method 3665) to remove GC/ECD interferences and analyzed for PCBs as the Aroclors, DDE, heptachlor, aldrin, DDMU, mirex, hexachlorobenzene, and some other chlorinated pesticides. These compounds are not acid labile. Note that certain pesticides were found in both fractions such as α-BHC and DDT. The second fraction, 100% fraction (100 % diethyl ether preserved with 2% ethanol) was cleaned up using a semi-micro acetonitrile partitioning step to remove lipids. This was split into two aliquots: one was for GC/ECD analysis after treating with concentrated sulfuric acid for the remaining non-acid labile chlorinated pesticides; the second fraction was eluted again with 100%

diethyl ether using micro Florisil® chromatography (SW-846 Method 3620A) for GC/AED analysis for the remainder of the target pesticides, which included organo-nitrogen, organo-phosphorus, and the remaining organo-chlorine pesticides. Note that these pesticides are acid labile.

During the second half of the project, the extraction and clean-up procedure was further streamlined. Extracts were split 50:50 with one portion archived in a refrigerator. The extracts for chlorinated pesticides/Aroclors listed in Appendix A, Table A-3 required Florisil® clean-up (SW-846 Method 3620A), generating two elution fractions using hexane/ethyl ether as the eluant system. The first fraction, 0% diethyl ether fraction (100% hexane), was treated with concentrated sulfuric acid (SW-846 Method 3665) to remove GC/ECD interferences and analyzed for PCBs as the Aroclors, DDE, Heptachlor, Aldrin, DDMU, Mirex, hexachlorobenzene, and some other chlorinated pesticides as above. These compounds are not acid labile. Note that there was a portion of certain pesticides that were present in both fractions such as a-BHC and DDT. The second fraction, 50% fraction (50 % diethyl ether preserved with 2% ethanol and 50% hexane) was cleaned up using either a micro acetonitrile partitioning step to remove lipids or directly treating with elemental mercury to remove sulfur followed by concentrated sulfuric acid. Both resulting extracts were treated with acid and analyzed by GC/ECD.

A portion of the archived extract was cleaned up using a micro acetonitrile partitioning step to remove lipids. This fraction was eluted with 100% diethyl ether using micro Florisil® chromatography (SW-846 Method 3620A) for GC/AED analysis for the remainder of the target pesticides, which included organo-nitrogen, organo-phosphorus, and the remaining organo-chlorine pesticides. Note that these pesticides are acid labile.

### 7.2.4 Acid-Labile Pesticides Using GC/AED and Method 8085

According to specifications in the QAPP **(1)** and considering the results of the chlorinated pesticide/Aroclor analysis and the location of project samples, the project manager and the project risk assessment manager selected a subset of project samples to be measured by EPA Method 8085. The subset included a few samples with low concentrations as well as samples with high chlorinated pesticide/Aroclor concentrations. Quantitation limits for AED target compounds listed in Appendix A, Table A-3 are unknown, because most of these compounds have not been previously measured in a fish matrix using Method 8085.

Method 8085 is applicable to the screening of semi-volatile organohalide, organophosphorus, organonitrogen, and organosulfur pesticides that are amenable to gas chromatography. The method is intended for screening samples for the presence of hetero-atom containing organic compounds, particularly for synthetic pesticides. Hetero-atoms in this case are defined as those elements in an organic compound other than carbon, hydrogen, and oxygen. Practical quantitation limits (PQL) were determined from a single point calibration. Measurements were made from a compound independent calibration (CIC) utilizing an AED elemental response that was not compound specific.

Sample extracts were analyzed by injecting a 1 to 2-ul aliquot into a gas chromatograph equipped with a wide-bore fused silica capillary column and an atomic emission detector

(GC/AED). The AED uses a microwave-induced helium plasma to generate temperatures in the detector that are high enough to break the molecular bonds of compounds that elute from the GC. The resulting free atoms undergo electron excitation, followed by relaxation and photoemission. These atomic emissions occur at frequencies characteristic of the element. The intensity of the atomic emission is proportional to the concentration of the element in the detector. In this method, the emission frequency and intensity were monitored for seven elements. The results are used for detection and, if multiple hetero-atoms are present, determination of the ratio of hetero-atoms present in the target compound.

The following two types of instrumental calibration are possible using Method 8085:

1. Compound Dependent Calibration (analyte calibration) -- A single point calibration of all target compounds at their respective practical quantitation limits (PQLs) is performed.

2. Compound Independent Calibration (CIC) -- The AED provides response to elements that are independent of compound structure, thus with CIC, elemental calibration is possible. This type of calibration using a compound of similar structure is referred to as CIC AERF. Hetero-atoms, sulfur, nitrogen, chlorine, bromine, iodine, and phosphorous (fluorine if needed) are calibrated using a compound independent calibration mixture, CIC mix. The elemental response factors obtained from this type of calibration are used to quantify individual hetero-atoms contained in any or all compounds eluting from the column, not necessarily to the specific target compounds. All hetero-atom quantitation is then translated to either target compound quantitation and/or to tentatively identified unknown compounds (TICs).

The sample clean-up procedure for AED extracts has been previously described in Section 7.2.3, above. One group of compounds measured in the AED fraction were polybrominated diphenyl ether (PBDE) isomers. As has been reported previous lin Section 7.2.1, PBDE isomers were also detected by AXYS Laboratory as an interference in the measurement of selected PCDDs/PCDFs. PBDEs have been used as fire retardants in the manufacture of polymers, wire, and cable coatings, electrical connectors, adhesives, polystyrene and polypropylene plastics, and butadiene rubber. The CAS number for one isomer, decabromodiphenyl ether is 1163-19-5. Some PBDEs have trade names such as Bromokal 82-ODE, Bromokal 70-5DE, Berkflam, Saytex 102E, and Tardex 80. A useful product internet site is *www.albemarle.com/saytexbroc.htm*. A recent journal publication in Archives of Environmental Contamination and Toxicology by Lindström, et. al. **(15)** provides a brief current review of the occurrence of these brominated contaminants in the blubber of a long-finned pilot whale. According to this publication, the 1992 world annual production of PBDEs was 40,000 tons. The use of PBDEs as a fire retardant in plastics is increasing each year.

In project AED extracts, PBDEs tended to elute between the 100% hexane and 6% diethyl ether/hexane Florisil® fractions. In order to perform an appropriate analysis, a separate clean-up technique was employed.

For Method 8085 AED analysis of project sample extracts, a Hewlett-Packard Model 5890 gas chromatograph interfaced to a Model 5921A atomic emission detector (AED) was used. The analytical column was a J&W 30m X 0.45 mm with a 0.43 μm DB-5 stationary phase film thickness. The samples were monitored for selected sulfur (181 nm), phosphorus (178 or 186 nm), nitrogen (174 nm), iodine (183 nm), bromine (478 nm) and chlorine (479 nm) containing compounds. EPA Method 8085 and the AED data validation report of 4/28/99 describe the calibration and analysis procedure which was used to measure AED pesticides. The typical quantitation limit (QL) for project samples was between 100 and 1000 ug/kg.

A target compound is identified by a positive response of the AED of at least one element contained in the compound at the proper chromatographic retention time. Confirmation of identity included a relative percent difference (RPD) of less than 20% for the empirical ratios of two included elements, the presence of three or more included elements, or by mass spectral (MS) identification. The absence of non-included elemental response may in some cases provide identity confirmation, but is generally less acceptable. If possible, all four techniques are used.

If a compound was adequately identified, but determined outside the calibration range or the calibration standard did not meet AED response criteria, the measurement value was considered an estimate and qualified as "J". Detected compounds that were not adequately identified, but show significant evidence of their presence in the sample were considered tentatively identified compounds (TICs) with estimated quantitation and were qualified with a "NJ" qualifier.

As mentioned, above, some samples contained polybrominated diphenyl ethers (PBDEs). These compounds tend to elute on the Florisil® column between the 100% hexane and 6% diethyl ether/hexane fractions. In order to perform an appropriate analysis, a separate clean-up technique was employed. The following is a summary of the procedure used for the preparation of samples for PBDE analysis:

> Twenty-five percent of the sample extract was diluted to 12.5 ml with hexane. The resulting extract was treated with concentrated sulfuric acid for one minute. About 10 ml of the solvent portion was transferred to another container and concentrated using a N-Evap to a volume of about 1 ml. That extract was quantitatively transferred to a one gram BakerBond® Florisil® cartridge and eluted with five milliliters of 6% diethyl ether (preserved with 2% ethanol) in hexane. The extract was then taken to a volume of 0.4 ml (equivalent extract volume of 2 ml) for analysis. Any lost of extract was accounted for and used to adjust the final extract volume to attain the same equivalent extract volume.

A retention time calibration curve was performed for the polybrominated diphenyl ether (PBDE) compounds which were prepared on 10/07/98. This standard was prepared in the laboratory by reacting bromine with diphenyl ether. The amount of PBDEs in project samples was calculated based upon the CIC AERF to bromine.

Abate, Diuron, Merphos, and Diclofol (Kelthane) were not analyzed directly, but were analyzed based on their breakdown product responses. Their quantification was therefore considered estimated and qualified as "UJ" when not detected, and qualified as "J", when detected.

Compounds having unacceptably low matrix spike recoveries (an average recovery of less than 30%) or poor precision (a RSD of greater than 35%) include:

> Simazine, Terbacil, Bromacil, Cyanazine, Norflurazon, Sulprofos, Dioxathion, Dichlorvos, Metribuzin, Captan, Captafol, Diuron, Phorate, Endrin Aldehyde, Carbophenothion, Fenthion, Mevinphos.

The quantification limits for these compounds are considered estimates and qualified as "UJ", when not detected, and qualified as "J", when detected.

Compounds not determined due to loss during Florisil/partition clean-up, having numerous present or past matrix recoveries of 0%, having calibration checks that failed to meet minimum signal-to-noise criteria during the course of analysis, or having insufficient data available to draw conclusions about their expected recovery include the following target compounds:

> Tebuthiuron, Atraton, Metalaxyl, Carboxin, Hexazinone, Fensulfothion, Dimethoate, Methyl Paraoxon, Phosphamidan, Dioxathion, Demeton-O, Demeton-S and Fluridone.

All of the data for the above, compounds are considered rejected and qualified as "R".

### 7.2.5 Neutral Semivolatiles

Neutral SV target compounds were measured in project samples using EPA Method 8270 with selected ion monitoring (SIM) to improve the sensitivity of the method. Target compounds selected by the QAPP **(1)** are listed in Appendix A, Table A-3. The typical instrument quantitation limit (QL) for project samples was between 4 and 50 ug/kg.

Extracts were cleaned up using either gel permeation chromatography (GPC) or Jordi-gel chromatography followed by silica gel column chromatography to isolate a neutral fraction containing PAHs and compounds. Target compounds were measured using HRGC/LRMS/SIM in order to achieve the quantitation limits listed in the QAPP **(1)**.

The Manchester Laboratory measured hexachlorobenzene by both GC/ECD (pest/PCBs) and by GC/MS (SVs), even though the QAPP (1) specified to use the more sensitive method -- GC/ECD. Hexachlorobenzene was a non-detect in all samples using GC/MS except 4 sturgeon composites and one steelhead. Hexachlorobenzene, by contrast, was measured in 182 composite project samples using the more sensitive method -- GC/ECD.

The recovery of N-nitosodiphenyl amine in MS/MSD samples by the Manchester Laboratory was less than 10% for most spiked samples. Therefore, all project measurements for N-nitosodiphenyl amine were qualified with an "R" qualifier (rejected for all uses).

### 7.2.6 Chlorinated Phenolics

The chlorinated phenolics listed in Appendix A, Table A-3 were extracted, derivatized by acetylation, and analyzed using a modification to the procedure described in draft Method 1653. The typical quantitation limit (QL) for project samples was between 400 and 1000 ug/kg.

A synopsis of the analytical procedure for the analysis of the chlorinated phenolics is as follows: A portion of the hexane extract prepared from the fish tissue was added to a stir-bar extraction vessel containing one liter of potassium carbonate buffer. Internal standard and surrogate compounds were added and the mixture stirred. Acetic anhydride and hexane were added and the mixture stirred to simultaneously derivatize and extract the derivatives. If necessary, extracts were cleaned up by either silica gel or alumina chromatography. Additional details are described in Manchester Laboratory SOP 730016-7/93.

### 7.2.7 Metals

Inductively coupled plasma/mass spectrometry (ICP/MS) is applicable to the determination of trace levels of a large number of elements in tissue samples. The typical instrument detection limit (IDL) for project samples was between 0.004 to 0.1 mg/kg, depending upon the metal measured. Acid digestion prior to filtration and analysis was required for project fish tissue samples. ICP/MS has been applied to the determination of over 60 elements in various matrices. A freeze-dried fish reference sample was measured with each group of project samples which were digested in order to provide laboratory quality control on overall analytical system performance.

A summary of the digestion procedure for project tissue samples is as follows: Samples were digested in batches of 20, which included a sample duplicate, matrix spike/matrix spike duplicate, method blank, and a “fish” reference material (freeze-dried dogfish sample). Five gram subsamples of homogenized fish tissue were transferred to 250 ml pre-cleaned Teflon beakers. Tissues samples were digested in a Class 100 hood as specified in EPA method 200.3. The addition of hydrochloric acid was omitted to avoid interferences produced by the chloride ion during ICP/MS analysis.

Hydrogen peroxide was added to a maximum of six milliliters and the multi-element spike was added to give a concentration of 30 ug/l in the analytical solution for each element. After a period of cooling, the samples were transferred to 125 ml polyethylene pre-cleaned bottles and diluted with ASTM type I water to 100 ml. Samples were then left to settle any insoluble material and then diluted five times with deionized water.

The reference material used was DORM-2, freeze-dried dogfish muscle and liver, from the National Research Council Canada (NRCC). The amount of DORM-2 digested was 0.5 grams.

Samples were analyzed as soon as possible after digestion by ICP/MS using the EPA method 200.8. Samples were measured against a linear, four-point calibration curve forced through the origin, and results were reported in mg/kg on a wet-weight basis.

The reference material was only analyzed as a measure of precision throughout the long term of project sample collection. DORM-2 is a different matrix than project fish samples and therefore is not representative of project digested frozen tissue. A frozen tissue reference sample was not available, therefore DORM-2 was the next best alternative.

Mercury measurements on project tissue samples are described in EPA Region 10 SOP "Automated Mercury Analysis of Tissue Samples by Cold Vapor Atomic Absorption (CVAA) Using Leeman Labs' PS200 or PS200ii, Revision 11/27/96."

Method 251.6, a cold-vapor atomic absorption method, is based on the absorption of radiation at the 253.7-nm wavelength by mercury vapor. The mercury in samples was reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passed through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance (peak height) was measured as a function of mercury concentration. The typical instrument detection limit (IDL) for project samples was between 0.03 and 0.05 mg/kg.

### 7.2.8 Radionuclides

Radionuclide analyses were performed by the EPA National Air and Radiation Environmental Laboratory (NAREL) in Montgomery, Alabama. NAREL is a comprehensive environmental laboratory managed by the U.S. EPA Office of Radiation and Indoor Air. Among its responsibilities, NAREL conducts a national program for collecting and analyzing environmental samples from a network of monitoring stations for the analysis of radioactivity. This network has been used to track environmental releases of radioactivity from nuclear weapons tests and nuclear accidents.

Project and QA requirements for the 45 samples (see Appendix A, Table A-1) selected for radionuclide measurements are described in the addendum QAPP, Radionuclide Measurements For QAPP For Assessment of Chemical Contaminants in Fish Consumed by Four Native American Tribes In the Columbia River Basin, Addendum Revision 2.0, September 3, 1997 **(2)**.

Radionuclide measurements of selected project samples have been completed and will be summarized in a separate volume to the project final report.

## 7.3 Calibration Procedures and Frequency

Calibration and frequency of calibration of laboratory instruments was performed according to the requirements of each method of analysis. Each laboratory used a Standard Operating Procedure (SOP) which describes how each target compound was measured.

## 7.4 Laboratory QC Procedures

Quality Control procedures specified in the QAPP and in the methods listed in Table 3 were followed and documented by each laboratory. In addition, Section 3.0 of the QAPP **(1)** specified that all quality control requirements of each method which is referenced in Table 3 shall be

obtained and reported by each analytical laboratory, which included QC requirements for surrogate compounds, internal standards, recovery standards, matrix spike compounds, calibrations, and method blanks. Compliance to these QC requirements were confirmed in each data validation report (see Appendix B, table B-4) for each target compound.

# Chapter 8.0 PROCEDURES USED FOR ANALYTICAL DATA VALIDATION AND DATA ASSESSMENT

## 8.1 Procedures Used For Validation of Project Data

This section describes data validation of project sample data, which is the process of technically reviewing analytical data using written data validation protocols, and qualifying measurement results using data qualifiers. The primary objective of validating project data was to determine if project data for each sample met the data quality objectives which were specified in the QAPP. After the data validation process was completed, data qualifiers were appended to measurement values by the data validation chemist. Final useability of qualified and validated data is determined by data users such as the Project Manager, CRITFC members, and local community members.

Data validation of PCDD/PCDF and dioxin-like, PCB data were conducted by EPA Region 10 using written protocols which have been previously described **(10,12)**.

EPA Region 10 Laboratory staff provided standard laboratory data validation of Region 10 Laboratory data using the following guidelines:

EPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review EPA 540/R-94/013 (PB-94-963502). **(13)**

EPA Contract Laboratory Program National Functional Guidelines for Organic Data Review EPA 540/R-94/012 (PB-94-963501). **(14)**

A total of 93 data validation reports were prepared detailing the quality of project data. These data validation reports are listed in Appendix B, Table B-4. All data validation reports were prepared according to the data validation guidelines specified in the QAPP **(1)**.

All QA and QC data from the measurement of both field and laboratory samples were used in assessing the quality of project data. Any project data which did not meet the stated requirements of the QAPP **(1)** or analytical method were qualified with appropriate data quality flags (see Appendices D, E, and F).

### 8.1.1 Data Quality Elements Used For Evaluation of Organics Data

Organics data for each sample were evaluated and determined to be acceptable for the following data quality elements:

- Holding Times and Sample Preservation

- GC/MS Tuning and Performance
- Initial Calibration
- Continuing Calibration
- Blanks
- Surrogate Spike Recoveries
- MS/MSD Samples
- Internal Standard Performance
- Target Compound Identification
- Tentative Identified Compounds
- Compound Quantitation
- Overall Assessment of Data

### 8.1.2 Elements Used For Evaluation of Inorganics Data

Inorganics data for each sample were evaluated and determined to be acceptable for the following data quality elements:

- Holding Time
- Sample Preparation
- Calibration
- Reference Control Samples
- Blanks
- ICP-AES Interference Check Sample
- ICP-AES Serial Dilution
- Matrix Spike Analysis

- Detection Limits

- Data Summary

Several data qualifiers used to validate the metals data were special qualifiers which were devised by the EPA Manchester Laboratory (see Appendix E). For example, the qualifier, "N", was defined as "spiked sample recovery results were not within control limits". This qualifier was sometimes used when a matrix spiked target compound was measured outside the project accuracy limits of 60% to 140% for MS/MSD samples. The "N" qualifier was given to arsenic values in 16 project samples (143% MS recovery) , to lead values in 14 project samples (180% and 102% MS recovery), and to selenium values (153% MS recovery) in 19 project samples. Project data users may decide to use these "N" qualified values, however, these "N" qualified values should be considered to be biased high and of estimated quantity. Since "N" qualifiers are not used for metals data according to data validation requirements of the QAPP **(13)**, "N" qualified arsenic, lead, and selenium data qualifiers have been changed to "J" qualified data in the project database.

For the validation of metals data, the Manchester Laboratory used the following definition for the qualifier "J": "The reported value is an estimate because of the presence of interference." The Manchester Laboratory qualified aluminum values with a "J" qualifier in 3 of the 14 groups of metals data validated by the Laboratory, due to the use of aluminum foil to wrap fish samples in the field. However, not all fish were wrapped in aluminum foil. The Laboratory did not have information on which samples were wrapped in aluminum foil and which samples were not wrapped in aluminum foil. Data users should be aware that project samples may be contaminated by the use of aluminum foil. Therefore, data users should be cautious in using project aluminum values. "J" qualified aluminum data which were qualified due to the possible use of aluminum foil to wrap project samples have been changed to non-qualified data ("J" removed) in the project database. CRITFC data users of metals measurements should use the CLP definition of "J" as was used for the mercury data, ie,

> "J" = The analyte was positively identified. The associated value is an estimated quantity.

## 8.2 Procedures Used For Data Quality Assessment

After the environmental data were collected and validated in accordance with the QAPP, the data were evaluated to determine whether the data quality objectives of the QAPP had been satisfied. EPA has developed guidance on Data Quality Assessment to address this need. Data quality assessment involves the following determinations:

- whether the data meet the assumptions under which the DQOs and the data collection design were developed;
- and whether the total error in the data was small enough to allow the decision maker to use the data to support the decision within the tolerable decision error rates desired by the decision maker.

Table 3 of the project plan **(1)** requires that precision and accuracy goals as are listed in the table be met. These precision and accuracy requirements are based upon the measurement of matrix spike and matrix spike duplicate (MS/MSD) samples. Table B-3 in Appendix B provides the results of precision measurements of project samples. Table 4 provides the summary of precision and accuracy measurements by group of target compounds measured. Tables B-3 and 4 show that the overall accuracy of MS/MSD measurements was 83%. The overall precision of MS/MSD measurements was 17%. All requirements of the QAPP for precision and accuracy of data were met.

In addition, the QAPP **(1)** required that 8 sets of blind field duplicate samples be measured to assess the precision of the entire sample collection, fish grinding and compositing, and analytical measurement system. Actually, 9 sets of blind duplicate samples were collected and measured (see Table B-2 in Appendix B). The following are the precision results (percent difference as is defined in the QAPP) for the measurement of 9 blind field duplicate samples:

- PCDDs/PCDFs = 21%
- Mercury = 13%
- ICP/MS Metals = 22%
- PCB congeners = 11%
- Chlorinated Pesticides/Aroclors = 20%

Overall Precision of 9 Field Duplicates = 18%

It should be noted that precision of field duplicate samples for other measurement groups could not be calculated because the measurement of target compounds in these groups provided primarily non-detect values.

The above results from the measurement of blind field samples show that the collection of fish, tissue grinding, compositing, and analytical processes resulted in acceptable precision for the entire system as was defined the QAPP **(1)**.

The design of the QAPP required the collection of triplicate composite samples at most sampling sites. The purpose of measurement of three samples at each site was to measure the variation of different types of samples at each sampling site. Table C-1 in Appendix C lists the average measured value and standard deviation of the first 10 composite groups. Appendix C, Table C-1 presents the precision of only the first 10 composite groups, because it would require 449 pages to print the precision of all replicate samples. Replicate precision results are also presented graphically in other volumes of the Final Project Report.

Finally, the QAPP required that 6 performance evaluation (PE) reference tissue samples be measured for PCDDs/PCDFs and PCB congeners. The first 3 PE samples were measured at the beginning of project. The last 3 PE samples were measured at the conclusion of the project. The results from the measurement of all 6 PE reference fish samples is reported in Table 5.

# Chapter 9.0 PERFORMANCE AND SYSTEM AUDITS

Selected performance and systems audits for field work and analyses were conducted according to the following schedule:

### 9.1 Audits Related to Sample Collection and Sample Filleting

The Project Field Operations Manager, Dave Terpening, was present during all sample collection and filleting field activities. Basic requirements stated in the QAPP **(1)** for sample collection, filleting, documentation, chain of custody, and shipping of project samples were met.

### 9.2 Audits Related to Grinding and Compositing of Fish Tissue

On September 6, 1996, the Field Operations Manager, Dave Terpening, conducted an on-site Technical Systems Audit of AXYS Laboratory in Sidney, B.C., which was responsible for grinding and compositing project fish samples. He was accompanied by the EPA Project Leader and Risk Assessor, Dana Davoli, the EPA QA Manager, Robert Melton, the CRITFC Project Consultant, Greg Glass, and by the TetraTech/EVS Project QA Manager, Tad Deschler. Even though the audit team determined that AXYS had the experience, procedures, and facilities to grind and composite project fish samples, the audit team did express concern that ½ HP OMAS Triticarne tissue grinder may not be powerful enough to process large quantities of big fish such as sturgeon. This initial concern became a problem during the period of the project when the ½ HP grinder needed to be replaced with larger tissue grinders.

Section 6.3 describes the process of replacing the original tissue grinder, a ½ horsepower (HP) OMAS Triticarne grinder, with a 2.0 HP and 3.0 HP larger capacity tissue grinders. During the three year period, the following tissue grinders were used to grind project fish:

- 0.5 HP OMAS Grinder, model: Triticarne
- 2.0 HP Berkel Grinder
- 3.0 HP Berkel Grinder, model TCA-32, serial number S2457

Possible contamination of project tissue samples with ether PCB congeners or especially metals was a concern, therefore each grinder was tested for contamination of samples by conducting an equipment rinsate test. The results of these rinsate tests are also presented in Section 6.3.

The QAPP required that AXYS Laboratory prepare a video tape for submission to EPA of fish grinding and compositing procedures at AXYS. This video was received and approved by the Field Operations Manager. Photographs were prepared by AXYS of each sample composite and these were submitted to EPA for inspection. The Field Operations Manager inspected and approved each of these photographs.

### 9.3 Audits Related to Sample Analyses

EPA project representatives, a technical representative of CRITFC, and a representative of Tetra Tech conducted an on site audit of the analytical subcontract laboratory, AXYS Laboratory on 9/6/96 in Sidney, BC. The audit team consisted of the EPA Project Leader and Risk Assessor, Dana Davoli, the EPA QA Manager, Robert Melton, the EPA Field Operations Manager, Dave Terpening, the CRITFC Project Consultant, Greg Glass, and by the TetraTech/EVS Project QA Manager, Tad Deschler. The audit team determined that AXYS had the experience, procedures, and facilities to measure project samples for PCDDs/PCDFs and PCB congeners using high resolution mass spectrometry and EPA Method 1613B and EPA Method 1668.

As part of QAPP requirements **(1)**, AXYS Laboratory procured and measured PE samples EDF-2524, EDF-2525, and EDF-2526 at the beginning and end of the project using Methods 1613B and 1668. It should noted that the 95% confidence level limits of the PE reference samples were established over ten years ago, before there were certified standards for most of the PCDD/PCDF and PCB congener target compounds and labeled isotope dilution standards. Therefore, 95% confidence level limits of the PE reference samples should be reestablished using current, certified, reference standards. The results of the measurement of PCDDs/PCDFs and dioxin-like, PCBs in these PE samples (see Table 5) were evaluated by the Project QA Manager and determined to be acceptable.

# Chapter 10.0 CORRECTIVE ACTIONS

Corrective actions taken during the sample collection and analysis phase of the project fall into two categories: 1) analytical or equipment malfunctions which could affect the ability of project staff or Tetra Tech/EVS to meet the stated requirements of the QAPP and 2) nonconformance or noncompliance with QA requirements set forth for the project.

Sample Alteration Forms and Corrective Action Forms were used during the project to document cases which required corrective action. These sample alteration and corrective action forms were submitted to the EPA project QA manager and were place in project files. In addition, each laboratory provided a Case Narrative with the Laboratory Analytical Report which specified any problems which occur during the measurement of project samples.

# Chapter 11.0 RESULTS OF DATA QUALITY ASSESSMENT EVALUATION

## 11.1 Project Objectives

Quality assurance/quality control (QA/QC) requirements for the project were specified in the QAPP **(1)**. For preparation of this report, the QAPP was reviewed in order to determine if project objectives and project data quality objectives had been met.

The above referenced QAPP states the following project objectives:

- Measure fish contaminant levels for species and fishing locations being utilized by CRITFC member Tribes to provide, in conjunction with the CRITFC fish consumption report, an assessment of fish consumption among individuals of the Columbia River Basin and these Tribes as an exposure route to residues of toxic waterborne chemicals.

- Use the information derived from the exposure assessment to estimate potential health risks to fish consumers in the Columbia River Basin.

The overall QA objective for analytical data was to ensure that data of known and acceptable quality are produced so that potential health risks to fish consumers in the Columbia River Basin can be estimated. Data quality objectives (DQOs) for the project are discussed in Table 3 of the QAPP **(1)**, in the attachments to the QAPP **(1)**, and in other sections of the QAPP. Project DQOs include:

- The selection of the appropriate chemical target compounds to be measured and the appropriate quantitation limits for these compounds, and,

- Analytical objectives as defined by measurement of *precision, accuracy, representativeness, completeness, and comparability* of quality assurance samples such as field duplicate samples, performance evaluation samples, and laboratory quality control samples. These QA samples were used to evaluate project data to determine if data meet the specified DQOs of the QAPP.

An additional QAPP objective was that all project data be validated using EPA data quality assessment guidelines to determine if each measurement met the QA and QC requirements of both the QAPP and the applicable analytical method. The result of this data validation process was the assignment of data qualifiers to selected project measurement values. A list of the data qualifiers used in the validation of project data is provided in Appendices D and E.

## 11.2 Project QA/QC Samples

Specific field duplicates were collected in order to demonstrate the integrity and precision of specific project samples.

Project DQOs required that all quality control (QC) requirements for the measurement of all project samples meet the stated QC specifications of each analytical method. These analytical methods required that the laboratory measure method blanks, matrix spike (MS) samples (inorganics), and matrix spike/matrix spike duplicate (MS/MSD) samples (organics).

All QA and QC data from the measurement of project samples were used in assessing the quality of project data (see Tables 4 and 5, and Appendix B). Any project data which did not meet the stated requirements of the QAPP or analytical method were qualified with appropriate data quality flags (see Appendices D and E).

## 11.3 Evaluation of Data Validation Reports

Data validation reports of project data are listed in Table B-4 of Appendix B.

The EPA Project QA Manager reviewed each data validation report for completeness and adherence to written EPA data validation guidelines. All project results were determined to have been correctly qualified in the data validation reports and in the sample measurement results.

In cases where more that one qualifier was placed upon the data, the most restrictive qualifier was used to qualify the measurement value.

In general, all project data which do not have an attached qualifier can be used to meet the objectives of the project and the corresponding QAPP. The usefulness of qualified data depends upon the severity of the qualifier, the nature of the sample, and the use of the data. The final usability of the data is determined by the use of the data and the data user.

# Chapter 12.0 RESULTS AND DISCUSSION

## 12.1 Survey Objectives

The Project Final Report represents the conclusion of a U.S. Environmental Protection Agency (EPA) study to assess chemical contaminant exposure from consumption of Columbia River fish by four Native American Tribes (Confederated Tribes of the Umatilla Indian Reservation, Confederated Tribes of the Warms Springs Reservation, Nez Perce Tribe, and Yakama Nation) and other people in the Columbia River Basin.

This current phase of the study (referred to as Phase II), consisted of evaluating tissue contaminant data representing resident and anadromous fish species that are typically caught by Tribal fisheries in the Columbia River Basin and consumed by Tribal members and other people in the Columbia River Basin. The information from both phases of this exposure study was used to assess the potential health impacts to people in the Columbia River Basin from consuming contaminants in Columbia River fish.

The objectives for Phase II, as discussed in the draft study design document, have been previously stated in Section 3.1. Sampling and analytical results as qualified in project data validation reports (see Appendix B, Table B-4) and as listed in project measurement databases provide the scientific basis from which a limited accomplishment of objective 1, above, can be determined.

## 12.2 Field Sampling Results

Chapter 4.0 of this volume lists the project objectives and requirements of EPA and Tribal members for the selection of collection sites, species collected, sampling dates, type of fish tissue, sizes of fish, and number of fish in composites. All of the field sampling for the project was coordinated and conducted by both EPA Region 10 and CRITFC Tribal members. Field sampling required adherence to the following specifications in the QAPP **(1)**:

- The collection of field samples which are representative of the fish consumed by Tribal members as is described in Phase I of the study,
- The responsibilities of each member of the field team,
- Study objectives and time commitments for the project,
- Collection permit requirements,
- Site locations and collection equipment and gear needed at each site,

- Proposed sampling dates and species of interest for each site location,
- Composite sample size for each species and sample type, and
- Fish handling procedures and storage requirements.

Actual sampling specifications required modification during the period in which project samples were collected due to environmental conditions in the field such as changes in weather, project resources, and fish populations. All changes in sampling specifications were discussed and coordinated with Tribal representatives. EPA is grateful to the many Tribal members who made the accomplishment of project sampling objectives a major success. As a result of the tremendous help and work of Tribal members and a dedicated EPA/Tribal sampling team, the overall sampling objectives of the QAPP were accomplished.

### 12.3 Homogenization of Individual Fish and Fish Composites

Section 6.0 of this volume provides a list of project objectives and requirements for the homogenization of individual fish and fish composites. Project records, photographs, and an examination of homogenized project samples at the EPA Manchester Laboratory indicated that these objectives and specifications were met by EPA and Tribal field staff members and by the tissue grinding and homogenization staff at AXYS Laboratory. The integrity and representativeness requirements of field samples as described in the QAPP (1) were met.

### 12.4 Selection of Project Target Compounds and Detection Limits

The selection of target compounds and the risk-based detection limit goals were determined in the draft study design document prepared for the project by Tetra Tech (3). In this document, target analytes were selected by considering guidance provided by EPA (4) and by performing a health risk-based screening analysis of tissue contaminant data collected within the Columbia River Basin during the last ten years (1984-1994).

As shown in Appendix A, Table A-3, several chemicals have detection limits that are above the risk level goals that were calculated. For this project, analytical methods were chosen to provide detection or quantitation limits which are as low as possible given available analytical methods and resources.

#### 12.4.1 Core Target Compounds

Due to lack of project resources, the following two groups of target compounds were not measured in all project samples: AED pesticides and radionuclides. A subset of project samples were chosen to measure AED pesticide target compounds and radionuclide target compounds, based upon a coordinated decision between EPA and Tribal representatives of the project. All target compounds in non-AED pesticide and radionuclide chemical groups are referred to in this QA volume as core target compounds. Core target compounds are those compounds listed in Appendix A, Table A-3, which are in the following chemical groups:

1. Dioxins/furans
2. GCP (chlorinated phenolics)
3. Mercury
4. ICP/MS metals
5. PCB congeners
6. Pest-PCBs (non-acid labile chlorinated pesticides and Aroclors)
7. SV (neutral semi-volatiles)

Core project samples are defined in this volume of the Final Report as those samples in which we have complete measurements for all target compounds in the above seven chemical groups. The total number of core project samples was 284 samples. These 284 samples provide the basis for the comparison of data of chemical contamination and risk assessment for the entire project.

### 12.4.2 Non-Core Target Compounds

Non-Core target compounds are those compounds listed in Appendix A, Table A-3, which are in the following two chemical groups:

1. AED-pesticides
2. Radionuclides

Non-Core project samples are defined in this volume of the Final Report as those samples in which we do not have complete measurements for all target compounds in the above, seven chemical groups listed in Section 12.4.1. The total number of core project samples was 284 samples. The total number of non-core project samples was 20 samples. These 20 samples can not be used to provide the basis for the comparison of data of chemical contamination and risk assessment for the entire project, because we have not measured all target compounds in these samples.

## 12.5 Selection of Analytical Methods

Chemical methods of analysis were chosen based upon the criteria listed in Section 5.1, and the instrumentation and analytical methods which were available when the QAPP was approved in 1996. Table 3 provides a list of the methods which were chosen for use on the project.

### 12.5.1 Established Analytical Methods

The following methods of analysis provided project data with the least number of qualified data points according to the data validation reports listed in Appendix B, Table B-4:

1. Method 1613B -- Dioxins/furans
2. Method 251.6 -- Mercury
3. Method 200.8 -- ICP/MS metals
4. Method 1668 -- PCB congeners
5. Method 8081 -- Pest-PCBs (non-acid labile chlorinated pesticides and Aroclors)

Target compounds measured using the above, five methods of measurement, provided data with the fewest number of qualified data points. Therefore, the measurement of these target compounds in the 284 core project samples provided the highest level of useable information for the calculation of comparative chemical contamination and comparative risk assessment. Measurements for PCDDs/PCDFs and PCB congeners were especially of high quality, according to the measurement of blind field duplicate samples and Reference PE samples. None of the PCDDs/PCDFs and PCB congeners measurements were qualified as estimated values ("J" qualified).

Data validation reports using the above methods of measurement listed a number of problems in the measurement of target compounds. For dioxins/furans, PCB congeners, and Pest-PCBs (non-acid labile chlorinated pesticides and Aroclors), the primary analytical problem encountered by the labs was the interference of chlorinated and brominated non-target compounds in extracts of project fish samples. For PCB congeners, AXYS Laboratory also found that many sample extracts had to be diluted and re-measured because of high levels of PCB congener target compounds in some sample extracts. Data validation reports for the measurement of ICP/MS metals and mercury indicate that, once the EPA Manchester Laboratory developed modifications to digestion procedures for high levels of lipids in some project samples, the use of Method 200.8 and 251.6 proceeded smoothly.

### 12.5.2 Non-Established Analytical Methods

The following methods of analysis provided project data with the largest number of qualified data points:

1. Method 1653 -- GCP (chlorinated phenolics)
2. Method 8270/SIM -- SV (neutral semi-volatiles)
3. Method 8085 -- AED/pesticides
4. NAREL SOPs -- Radionuclides

Data validation reports show that Methods 1653, 8270/SIM, and 8085 provided organics data which had relatively high quantitation limits.

## 12.6 Validation of Project Data

As was required in the QAPP **(1)**, all project data were scientifically examined for assessment of data quality by undergoing a formal data validation process (see Appendix B, Table B-4). The validation of data in the following chemical groups was relatively unambiguous, because written data validation guidelines were either previously available, or, were written specifically for the project:

1. Method 1613B -- Dioxins/furans
2. Method 251.6 -- Mercury
3. Method 200.8 -- ICP/MS metals
4. Method 1668 -- PCB congeners
5. Method 8081 -- Pest-PCBs (non-acid labile chlorinated pesticides and Aroclors)

6. Method 1653 -- GCP (chlorinated phenolics)
7. Method 8270/SIM -- SV (neutral semi-volatiles)

The validation of data in the following chemical groups was relatively difficult, because written data validation guidelines were not available and analytical methodology for the analysis of fish samples using these methods was not well established:

1. Method 8085 -- AED/pesticides
2. NAREL SOPs -- Radionuclides

However, all project measurements were correctly qualified according to the written data validation guidelines cited and used by the assigned data validator. Data users should review each specific data validation report for information regarding the limitations in the use of project data. For example, in project composite sample 98174085 (smallmouth bass, WB, Yakama River at site 48D), ethyl chlorpyrifos was measured at 43 ug/kg with a "J" qualifier. The MS/MSD for this composite sample showed that the average percent recovery for ethyl chlorpyrifos was 71%. Therefore, MS/MSD recovery results indicate that the amount of ethyl chloropyrifos present in the fish composite may be higher than 43 ug/kg as is reported in the project database.

## 12.7 Target Compounds Which Have Not Been Previously Reported In Columbia River Basin Fish

Preliminary studies indicate that there were several target compounds which were measured in project samples which have not been previously reported as being present in Columbia River Fish. Table 9 provides a list of these newly reported target compounds. Most of the new target compounds are PCB congeners measured by Method 1668, AED-pesticides measured by Method 8085, and SV target compounds measured by Method 8270. Among the 24 newly measured target compounds reported in Table 9, five are pesticides, three are brominated diphenyl ether fire retardant isomers, ten are PCB congeners, and six are semivolatile compounds. Generally, the measurement of these new target compounds are due to the use of new analytical methods and the use of newly developed sample extract clean-up procedures.

## 12.8 Accomplishment of Project QA and QC Analytical Objections

The objectives of the QAPP required a high level of communication and teamwork among EPA and Tribal project members. Because the length of the sampling period and analytical work extended over a three year period, procedures for collection of samples, grinding and compositing of fish, and the analysis of target compounds had to be consistent in order to develop a comparable database of chemical measurements. Precision from the measurement of blind field duplicate samples and precision and accuracy from the measurement of MS/MSD samples indicate that the project team was successful in meeting analytical objectives of the QAPP.

Project quality assurance measurements and laboratory quality control measurements indicate that project data as have been qualified in project data validation reports are fully useable to assess

chemical contaminant exposure from consumption of Columbia River fish by Tribal members and other fish consumers in the Columbia River Basin.

**Table 9. Target Compounds Which Have Not Been Previously Reported As Identified In Columbia River Basin Fish**

| ANALYTICAL METHOD | CHEMICAL GROUP | CAS NUMBER | CHEMICAL |
|---|---|---|---|
| EPA 8085 | AED-Pest | 5598130 | Chlorpyrifos-ethyl |
| EPA 8085 | AED-Pest | 90982 | Dichlorobenzophenone |
| EPA 8085 | AED-Pest | unknown | a Hexabromodiphenyl ether isomer |
| EPA 8085 | AED-Pest | 40487421 | Pendimethalin |
| EPA 8085 | AED-Pest | unknown | a Pentabromodiphenyl ether isomer |
| EPA 8085 | AED-Pest | 2312358 | Propargite |
| EPA 8085 | AED-Pest | unknown | a Tetrabromodiphenyl ether isomer |
| EPA 1668 | PCB congener | 74472-37-0 | PCB 114 |
| EPA 1668 | PCB congener | 31508-00-6 | PCB 118 |
| EPA 1668 | PCB congener | 65510-44-3 | PCB 123 |
| EPA 1668 | PCB congener | 38380-08-4 | PCB 156 |
| EPA 1668 | PCB congener | 69782-90-7 | PCB 157 |
| EPA 1668 | PCB congener | 52663-72-6 | PCB 167 |
| EPA 1668 | PCB congener | 32774-16-6 | PCB 169 |
| EPA 1668 | PCB congener | 35065-30-6 | PCB 170 |
| EPA 1668 | PCB congener | 35065-29-3 | PCB 180 |
| EPA 1668 | PCB congener | 39635-31-9 | PCB 189 |
| EPA 8081 | Pest-PCB | 1022226 | DDMU |
| EPA 8270/SIM | SV | 606202 | 2,6-Dinitrotoluene |
| EPA 8270/SIM | SV | 83329 | Acenaphthene |
| EPA 8270/SIM | SV | 191242 | Benzo(g,h,i)perylene |
| EPA 8270/SIM | SV | 193395 | Indeno(1,2,3-cd)pyrene |
| EPA 8270/SIM | SV | 90120 | Naphthalene, 1-methyl- |
| EPA 8270/SIM | SV | 483658 | Retene |

# Chapter 13.0 CONCLUSIONS AND RECOMMENDATIONS

## 13.1 Conclusions

As a result of the tremendous help and work of Tribal members and a dedicated EPA/Tribal sampling team, the overall sampling objectives of the QAPP were accomplished. Overall, this project for the assessment of chemical contaminants in fish consumed by Tribal members and other people in the Columbia River Basin has been a success, because the ambitious objectives of the QAPP have been accomplished. This project has produced a body of comparative chemical data which can be used by Tribal Members, risk assessors, public health agencies, and other interested parties to assess chemical contaminant exposure and risks from consumption of Columbia River fish.

## 13.2 Recommendations for Future Studies

Regarding the design and implementation of the QAPP **(1)**, there are several recommendations that may be useful for similar future projects:

1. Future projects of this nature should require the measurement of blind field duplicate samples at a frequency of at least 1 per 20 field samples. Calculations of precision from the resulting blind field duplicate data provide an important estimate of the variation of project measurements for the entire sample collection/sample measurement system. The measurement of blind field duplicate samples and laboratory matrix spike samples for this project provided data users with a degree of confidence in the useability of project measurement data.

2. It is suggested that future projects send field samples to a laboratory which performs only the fish grinding and compositing procedure and which does not conduct any target compound measurements. These composited samples could be sent by the fish grinding laboratory to the EPA Laboratory for separation by the project field operations manager into blind field duplicates which are prepared by splitting selected, homogenized fish composite samples into two portions and assigning separate field sample numbers to each portion of the homogenized fish composite. From the EPA laboratory the project field operations managers could send out normal project field samples and blind duplicate samples to the laboratories which are responsible for analytical measurements. This process would provide more comparative blind field duplicate samples for determination of precision of the field sampling/tissue grinding/composition/analytical measurement system. This project used a system of grinding right side and left side fillets to generate normal and blind field duplicate samples.

3. The measurement of lipid-soluble target compounds in heterogenous field samples such as fish samples presents special analytical problems, especially for the measurement of organic target compounds which tend to concentrate in the fat of biological species. Improvements need to be implemented in tissue grinding procedures and analytical extraction/digestion procedures in order to improve precision of analytical results. More research is required in order to provide better precision in analytical measurements. For example, most current analytical methods require extraction of a 5 to 10 g sample of fish tissue. The homogeneity of 10 g of ground fish tissue which has been passed through a meat grinder can vary considerably, depending upon the nature of the tissue sample and the grinding procedure and equipment used. This project attempted to minimize variability of organic measurements by specifying the procedure that the fish grinding laboratory was required to use and by closely monitoring to homogeneity of composite samples produced by the fish grinding laboratory. It is suggested that researchers working in the area of grinding and compositing biological tissue samples develop a more comprehensive procedure for improving the homogeneity of biological tissue samples. This new research may require the use of the current grinding procedures, followed by removal of a 200 g sample of ground tissue and ultra homogenization of this 200 g sample into a liquified sample using a ultra high-speed tissue homogenizer.

4. Additional work is needed to provide sources of native and labeled PCB congener standards which can be used for Method 1668 measurements. As is discussed in Section 7.2.2 of this QA Volume, PCB congener data validation reports for the project indicate that the purity of some of the native PCB congeners is uncertain.

5. EPA needs to develop data validation guidelines for high resolution mass spectrometry measurements of PCDDs/PCDFs and PCB congeners. EPA Region 10 has developed and posted on the EPA Region 10 homepage data validation SOPs for this purpose, however, EPA as a regulatory agency requires consensus guidelines for the validation of PCDD/PCDF and PCB congener data.

6. EPA Method 1668 for the measurement of dioxin-like PCB congeners does not list PCB 81 as a target compound. Therefore, this congener was not measured in project tissue samples. Congener PCB 81 is on the most recent WHO list of toxic PCB congeners and it should be added by EPA to the list of Method 1668 target compounds as soon as possible.

7. 2,3,7,8-TCDF measurements in project samples may not be comparable to 2,3,7,8-TCDF measurements in previous tissue samples from the Columbia River basin because much of this older data were not validated and measurements of 2,3,7,8-TCDF may not have been measured on a secondary GC column.

8. Additional resources are required by U.S. EPA to validate and finalize Method 1668 for the measurement of dioxin-like PCB congeners. Data from this project demonstrate the need for U.S. EPA to finalize and promulgate this important analytical method.

# Chapter 14.0 REFERENCES

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3. USGS 1993. Persistence of the DDT Pesticide in the Yakima River Basin Washington, U.S. Geological Survey, Circular 1090.

4. CRITFC, 1994. A Fish Consumption Survey of the Umatilla, Nez Perce, Yakama, and Warm Springs Tribes of the Columbia River Basin. CRITFC Technical Report No. 94-3. Portland, Oregon.

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15. Lindström, G., et. al., 1999. Identification of 19 Polybrominated Diphenyl Ethers (PBDEs) in Long-Finned Pilot Whale (Globicephala melas) from the Atlantic, Arch. Environ. Contam. Toxicol. 36, 355-363.

# APPENDICES

# Appendix A: PROJECT FIELD SAMPLING RESULTS

# Appendix B: PROJECT QA/QC RESULTS

# Appendix C: PRECISION OF PROJECT REPLICATE SAMPLES

Table C-1. Measurement of Precision In Project Replicate Composite Samples

# Appendix D: DATA QUALIFIERS USED TO VALIDATE ORGANICS DATA

The following qualifiers were used for organics measurement data attached to this Report:

**U** - The analyte was analyzed for, but was not detected above the sample quantitation limit. The associated numerical value is based upon the lowest calibration point of the 5-point initial calibration curve and any dilutions which were made to the sample due to high concentrations or matrix effects.

**J** - The analyte was analyzed for and was positively identified, but the associated numerical value may not be consistent with the amount actually present in the environmental sample. The data should be seriously considered for decision making and are useable for many purposes.

**R** - The sample results are rejected due to serious deficiencies in the ability to analyze the sample and meet quality control criteria. The presence or absence of the analyte cannot be verified.

Resampling and reanalysis are necessary to confirm or deny the presence of the analyte.

**UJ** - The analyte was analyzed for and was not detected above the reported quantitation limit. However, the reported quantitation limit is approximate and may or may not represent the actual limit of quantitation necessary to accurately and precisely measure the analyte in this sample.

**N** - The analysis indicates the presence of an analyte for which there is presumptive evidence to make a tentative identification.

Confirmation of the analyte requires further analysis.

**NJ** - A combination of the "N" and the "J" qualifier. The analysis indicates the presence of an analyte that has been "tentatively identified" and the associated numerical value represents its approximate concentration.

# Appendix E: DATA QUALIFIERS USED TO VALIDATE METALS DATA

The following qualifiers were used for metals measurement data (not mercury) attached to this Report:

**U** - Element was analyzed but not detected. The associated numerical value is the instrument detection limit/method detection limit.

**J** - The reported value is an estimate because of the presence of interference. An explanatory note is included in the data validation report.

**N** - Spiked sample recovery results were not within control limits.

**UJ** - Element was analyzed for, but was not detected. The associated numerical value is an estimate and may be inaccurate or imprecise.

# Appendix F: DATA QUALIFIERS USED TO VALIDATE MERCURY DATA

The following qualifiers were used for mercury measurement data attached to this Report:

**U** - The analyte was not detected at or above the reported result. The associated numerical value is the method detection limit, as defined in 40 CFR Part 136, Appendix B.

**J** - The analyte was positively identified. The associated numerical result is an estimate.